REDUCTION OF THE SULFUR CONTENT OF CERTAIN HIGH BOILING PETROLEUM FRACTIONS

By

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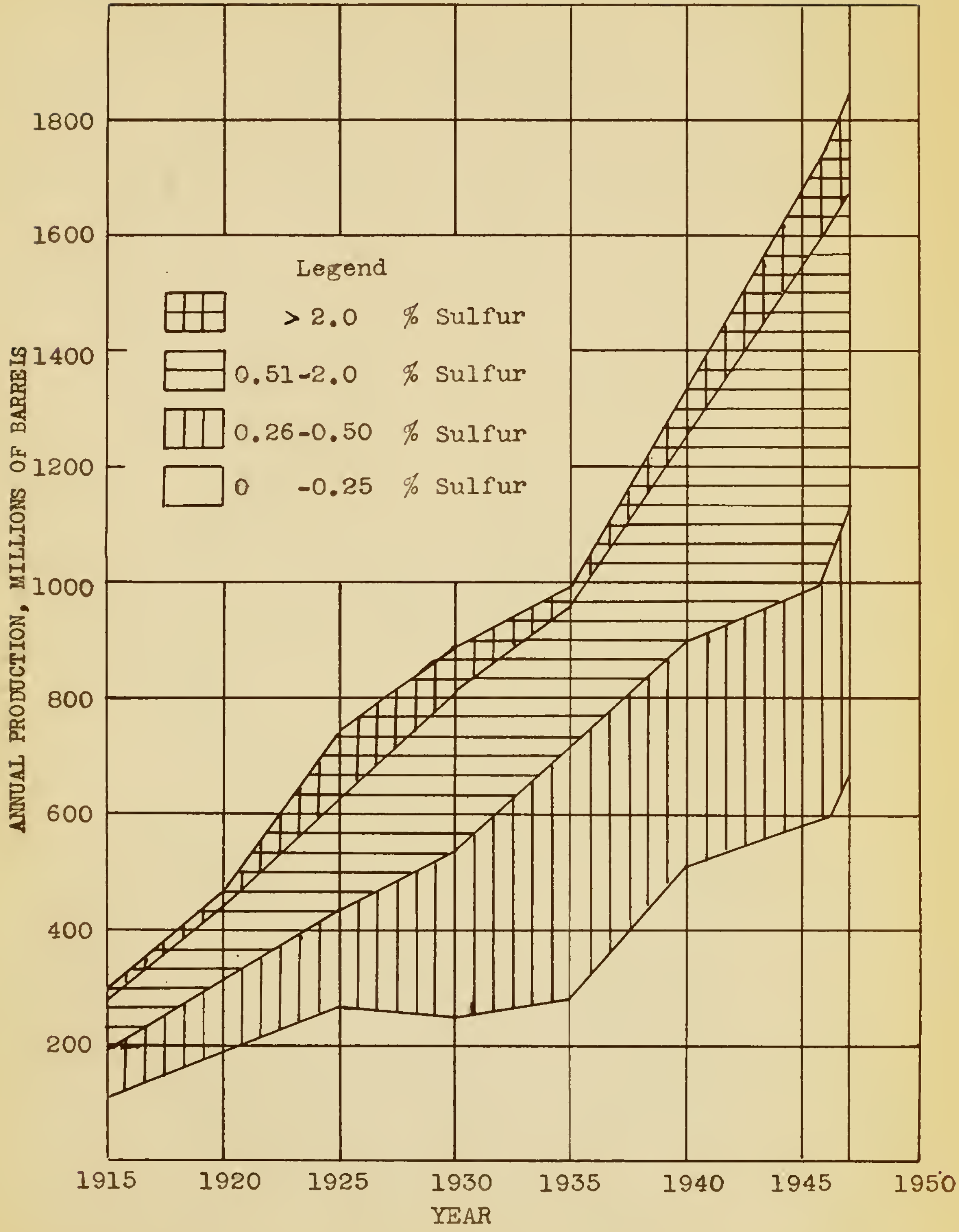
I. INTRODUCTION

For many years the petroleum industry has been faced with the problems imposed upon it by the presence of various types of sulfur compounds in crude oils processed in the refineries. The need for effective methods for removing sulfur from oils constantly is growing greater for several reasons. As the reserves of low-sulfur crude oils decrease, the refiner is forced to use more and more of the high-sulfur crudes in order to maintain or increase the amount of his products. Even for those refiners who have been processing sour crudes for a number of years, the increase in sulfur content of the refinery charge stocks has magnified and multiplied the number of problems normally encountered. In Figure 1 are plotted curves, published originally by Smith and Blade (23), and subsequently revised by them (22), showing the production of crude oils of various sulfur contents in the United States during the period from 1915 to 1947. As of the end of 1947, approximately 152 million barrels of the 1,863 million barrels of crude oil produced annually in the United States contained over two per cent sulfur and over 670 million barrels contained over 0.5% sulfur. The increased production of high-sulfur crudes in the Middle East and South America has added to the problem considerably since it appears that most of Europe's future requirements must necessarily be supplied

Figure 1

Crude Oil Production for the United States



from these sources. The large reserves of shale-oil located in the western parts of the United States and Canada are also high in sulfur content. Before these oils can assume the importance which is forecast by the large reserves available, a satisfactory solution to the sulfur problem must be obtained.

Several of the most important problems due to the presence of sulfur compounds in petroleum are (12):

1. Corrosion of refining, storage and transportation equipment.
2. Elimination of odoriferous sulfur compounds from products.
3. Depression of octane ratings.
4. Reduction of lead susceptibility.
5. Increased wear rates of engines.
6. Catalyst poisoning during catalytic processing of the crude oil cuts.
7. Adverse effects on product stability and burning characteristics.

Although the presence of sulfur causes many crude oils to be classified as "marginal" because of the above undesirable characteristics, the petroleum industry is finding it necessary to use such petroleums to satisfy present needs. Thus, the need for fundamental research on the removal of sulfur from petroleum products is becoming greater as the industry is forced to call upon all available resources to meet the demand for petroleum products.

A great number of studies have been made on the types of sulfur compounds found in petroleum and shale oils but it is apparent from a study of the literature that a large amount of fundamental information is still lacking. There is considerable disagreement as to the types of sulfur compounds that may occur in crude oils and straight-run distillates. There is also some question as to whether the types that are known to be present occur as such in the original petroleum or are formed during distillation.

A summary of the available knowledge on the occurrence of various types of sulfur compounds in oils is shown in Table 1 (8, 12). From these data several generalizations can be made. The presence of thiols (mercaptans) and disulfides is well established, with saturated compounds predominating in straight run distillates and aromatic derivatives predominating in cracked distillates. No aromatic sulfides have been isolated; probably due to the fact that the first member of this series has a relatively high boiling point. The presence of thiophenes in straight-run distillates is questionable, but their presence in cracked distillates has been well established. No compounds containing more than one sulfur atom to the molecule, other than disulfides, have as yet been isolated from petroleum sources (8).

The methods for removal of sulfur from petroleum oils may be separated into two types; those which remove the entire molecule containing the sulfur and those which remove only the sulfur. In general, the first type of process is

Table 1

Sulfur Compounds in Oil

	Type Formula	Crude	Straight Run	Cracked
Sulfur	S	+	+	+
Hydrogen Sulfide	H_2S	+	+	+
Mercaptans				
Aliphatic+	RSH	+	+	+
Naphthenic	RSH	-	-	-
Aromatic	RSH	?	-	+
Sulfides				
Aliphatic	RS-R	?	+	+
Naphthenic	R-S-R	?	+	?
Aromatic	R-S-R	-	-	-
Disulfides				
Aliphatic	R-S-S-R	?	+	-
Aromatic	R-SS-R	?	-	+
Thiophene and homologs	$\underbrace{S-CH=CH-CH=CH}$	?	?	+
Polysulfides	$R-S_n-S-R$	-	+	+

+ Sulfur Compound Present
- Sulfur Compound Absent
? Unknown or Questionable

used for light distillates and the latter for desulfurization of gas oils. This is due to the fact that it is important from the refiner's standpoint that the sulfur be removed in such a manner that the volume of the oil being desulfurized is not markedly reduced. In the case of the light distillates where the average number of carbon atoms per molecule is approximately six, the sulfur atom comprises a large part of the molecular weight. Thus the whole molecule can be removed without appreciably affecting the volume. In the case of the gas oils, the number of carbon atoms per molecule is in the range of thirty to sixty and an oil having five weight per cent sulfur content may contain twenty-five to fifty per cent sulfur compounds (12). Removal of the sulfur compounds as such would be economically unattractive in this case.

The entire sulfur compound may be removed by caustic washing, acid treating (1), or extraction with hydrogen fluoride (14). At the present time the only method known for complete desulfurization of petroleum oils by removing only the sulfur is some form of catalytic hydrogenation in which the sulfur is removed as hydrogen sulfide and the remainder of the sulfur bearing molecule is converted to a hydrocarbon. Essentially all of these processes are similar, with the operating conditions varying according to the type of catalyst used. Data have been published on such catalysts as fuller's earth (1), nickel-tungsten sulfides (4), nickel-molybdenum sulfides (23), bauxite (9), cobalt molybdate (2), and zinc-molybdenum bauxite (9). Of these catalytic methods, the cobalt molybdate process is the one most completely explained in the literature.

II. STATEMENT OF THE PROBLEM

There were two purposes of this investigation. The first was to determine how the sulfur content of the gas oil fractions of a variety of crude oils is distributed among the paraffin, naphthene, and aromatic fractions. The second purpose was to determine the manner in which the desulfurization by hydrogenation affects the distribution of sulfur.

The investigation was divided into two phases; one of analysis and the other of desulfurization.

The separation of the gas oils into their paraffin, naphthene, and aromatic components was accomplished by use of the chromatographic adsorption method developed by the United States Bureau of Standards. The sulfur content was determined by use of the high temperature combustion-titration procedure adopted by American Society for Testing Materials.

The gas oils were desulfurized by the low pressure hydrogenation method developed by the Union Oil Company which uses a cobalt-molybdate catalyst. Operating conditions were selected within the range of their development data in order that the effect of the change of operating variables would be known. All samples were desulfurized at the same operating conditions.

III. LITERATURE REVIEW

A. Chromatographic Adsorption

The method of adsorption used to separate petroleum fractions into their various molecular types is essentially that devised by the Russian botanist M. Tswett and is commonly known as the Tswett method or the chromatographic method. Previous applications of this method to the separation of aromatic hydrocarbons involved principally hydrocarbons of high molecular weight and of biological importance. Work by Mair and associates showed that fractionation by adsorption could be used to obtain separation of petroleum fractions in the gasoline (15), kerosine (16, 17), and gas oil (19) ranges into their molecular types of compounds.

The adsorption method consists, in general, of adsorbing the material to be separated on a suitable adsorbant, usually silica gel, then a suitable desorbing liquid is introduced. The desorbing liquid forces the hydrocarbon portion down the column of adsorbent causing the hydrocarbon portion to be fractionated according to the adsorbability of the various components. These components issue from the bottom of the column in the following order: Paraffin, naphthene, and aromatic.

The successful application of this technique requires a desorbant that will quantitatively remove the hydrocarbon from the adsorbent. Gooding and Hopkins (7) have pointed out that the characteristics desirable in a desorbant are:

1. A strength of adsorption greater than any component of the sample
2. A viscosity higher than that of any component of the sample
3. Complete miscibility with the aromatic portion of the sample
4. A refractive index sufficiently different from the aromatic portion that the final break on the adsorptogram may be determined satisfactorily.

When separating petroleum fractions in the gas oil range, it is virtually impossible to find a desorbant fulfilling completely all of the requirements. Desorbants used for this purpose are ethanol (13), cyclohexanol (19), 1-octanol (5), and n-henanol (19).

Reduction of the time required for analysis by raising the temperature at which it is conducted is desirable and it may be necessary to use an elevated temperature in the case of a gas oil having a high pour point. Analyses made by the same procedure on the same samples at room temperature and at 70°C. showed no significant difference (5). However, it was found necessary to maintain relatively close control of the temperature of operation in order to prevent remixing of the components.

Liquids which serve as desorbants or developers may be classified into two groups depending upon their strength of adsorption in relation to the material being separated (3).

The desorbants which displace adsorbed material from the column by virtue of their greater strength of adsorption are called displacents. In such an operation, the desorbed material is caused to move down the column ahead of and at the same rate as the displacent. The less strongly adsorbed developers are termed eluents. They will displace the paraffin and naphthene hydrocarbons but not the aromatic hydrocarbons. The paraffins, naphthenes, and eluent are obtained as a mixture from which the eluent is separated by distillation. The aromatic portion is then removed from the adsorbent by use of a displacent.

The size and shape of the adsorption column is specified by the Bureau of Standards (15) as well as the optimum size of silica gel to be used (17). The procedure used is similar to that of Mair, Sweetman and Rossini (18, 19) for the separation of gas-oil and wax fractions of petroleum. Almost any polar liquid which does not react with the hydrocarbons, the adsorbent, or the material of the adsorption tube may be used to displace the hydrocarbon material. It is also desirable that the desorbing liquid be completely soluble in water and preferentially less soluble in the hydrocarbon, in order that its removal from the hydrocarbon may be readily effected by extraction with water (16). Water easily displaces the aromatic hydrocarbons but they remain entrapped within the microscopic interstices of the adsorbent. For these reasons the Bureau of Standards recommends that methanol, ethanol, n-hexanol, or cyclohexanol be used as displacents (16, 18, 19). As the desorbed material issues from the bottom of the column, it is separated into samples of approximately 5 c.c. each. The refractive indices are determined on each of the samples and are plotted versus the amount of liquid collected. From this adsorptogram the amount of paraffins, naphthenes, and aromatics may be determined (19).

Fortunately, the breaks between various plateaus on adsorptograms for petroleum distillates are generally sharp, showing a reproducibility for the various groups of about two per cent (5). The separation within the aromatic group of monocyclic and dicyclic coumpounds may be sufficiently good to permit individual estimation of these classes (7).

B. Desulfurization Method

A review of the literature in regard to the desulfurization of gas oil by hydrogenation revealed that the only process on which comprehensive data have been published uses a cobalt-mobybdena catalyst (12). The oil to be processed is fed to a suitable preheating zone, mixed with hydrogen and then passes over the catalyst. Conversion of the sulfur compounds to hydrogen sulfide and hydrocarbons occurs either in the liquid or vapor phase. The effluent from the reactor passes through a condenser into a suitable system of gas-separators and product receivers. The liquid product is freed of hydrogen sulfide by caustic washing or distillation.

The operating conditions used for desulfurization depend on the characteristics of the stock being processed and the degree of desulfurization desired. Usually the conditions are in the ranges 600-850°F. catalyst temperature, 0.5-10.0 liquid hourly space velocity feed rate, 150 psig. or more, and with the circulation of 1,000 to 10,000 cubic feet of hydrogen per barrel of feed (12).

In excess of 1500 liquid volumes of feed have been desulfurized by one volume of catalyst without regeneration and without detectable loss in activity (2). The catalyst can be regenerated repeatedly to its original activity. Regeneration is accomplished by controlled oxidation to remove the carbon, Simultaneously, any metallic sulfide present in the catalyst is converted to oxide. These reactions generate a large quantity of heat and particular care must be taken to prevent local overheating of the catalyst which might cause shattering, sintering or other deleterious changes in physical structure (2).

The cobalt-molybdena catalyst is made by absorbing suitable cobalt and molybdenum salts in hydrous or dried aluminas (11). The coprecipitated catalyst is prepared by adding a water solution of cobaltous nitrate to some well stirred hydrous alumina followed by an ammoniacal solution of molybdenum trioxide. After washing, the gel is dried at 200°F., crushed, mixed with a suitable pelleting lubricant, pelleted, and then calcined for several hours at 1100°F. Alternately the cobalt and molybdenum salts may be absorbed in dried alumina pellets or beads, dried, and calcined.

Cobalt molybdate may be considered a chemical union of cobalt oxide and molybdic oxide, $CoO.MoO_3$. A comparison of the results of tests using each oxide separately and in physical mixtures as catalysts reveals that neither oxide, alone or in mechanical admixture, approaches the activity of the chemical combination (2).

The mechanism of the desulfurization is not known. Available evidence indicates that in the case of thiophene strong adsorption of the compound on the catalyst occurs followed by hydrogenation to thiacyclopentane. The ring then hydro-ruptures to give butyl mercaptan which may lose hydrogen sulfide to yield an olefin. The olefin is hydrogenated to a saturated hydrocarbon (12).

Hendricks, Huffman, Parker, and Stirton (11), have published results of the catalytic desulfurization of petroleum distillates which show the effect on the amount of desulfurization of varying space velocity, pressure, temperature and hydrogen rate. Previous work by Byrns, Bradley, and Lee (2) indicated that in the case of most of the compounds considered, 650°F. represented a rather critical temperature. If the catalyst temperature was decreased much below this figure, there was a rapid decline in activity with a resultant decrease in the degree of desulfurization. A more or less constant desulfurization activity was exhibited at temperatures between 650°F. and 800°F. with little or no evidence of hydrocarbon decomposition. However, catalyst activity was maintained over a much longer interval at 650°F. to 700°F. than at more elevated temperatures. For this reason they selected 650°F. as the most desirable temperature for operation.

The results of Hendricks and associates (11) show that doubling the feed rate (from 1.0 to 2.0 L.H.S.V.) approximately doubles the product sulfur (from 0.015 to 0.030 weight per cent).

An increase in pressure from 150 to 250 pounds per square inch gage results in considerably increased desulfurization (from 0.060 to 0.015 weight per cent).

Increasing the hydrogen rate from 3000 to 6000 cubic feet per barrel of feed causes a small increase in product sulfur (from 0.015 to 0.025 weight per cent) which was probably due to the decrease in contact time of hydrocarbon feed and catalyst.

The gas oil charge used in their investigations contained 2.28 weight per cent sulfur and was taken from Santa Maria Valley crude oil in regular refinery operations.

C. Analysis for Sulfur

The method employed for the analysis of sulfur in the various petroleum fractions is according to American Society for Testing Materials method of test E 30-46 T. The procedure used is as noted under "Organic Materials in General". The chemistry of the method is illustrated by the following reactions:

$$KIO_3 + 5KI + 6HCl = 3I_2 + 6KCl + 3H_2O$$

$$SO_2 + I_2 + 2H_2O = H_2SO_4 + 2HI$$

$$0.5\ S = I$$

IV. DESCRIPTION OF APPARATUS

A. Desulfurization Unit

The desulfurization unit consists of a feed tank, liquid feed rotameter, hydrogen feed rotameter, feed preheater, reactor, cooler, product tank, scrubbers, and wet gas meter together with temperature indicator controllers for the preheater and reactor and the necessary pressure control apparatus. A picture of the apparatus is shown in Figure 2 and a flow diagram in Figure 3.

The feed and product tanks are identical in construction. They are fabricated from three inch extra heavy steel pipe and equipped with Jergens reflex type liquid level gages. The tanks are 16 inches in outside length and have a capacity of 2500 cubic centimeters. Both tanks are wrapped with a 0.25 inch copper tube through which steam is passed to maintain the temperature of the liquid at 200°F. The tanks are insulated with Johns-Mansville asbestos shorts. They were hydrostatically tested at 800 pounds per square inch gage.

The liquid feed rotameter is a Schutte and Koerting 0.5 inch armored rotameter having an average flow capacity of 1000 cubic centimeters per hour. It was designed for viscous petroleum liquids and is equipped with three rotors in order that a wide range of viscosities may be covered.

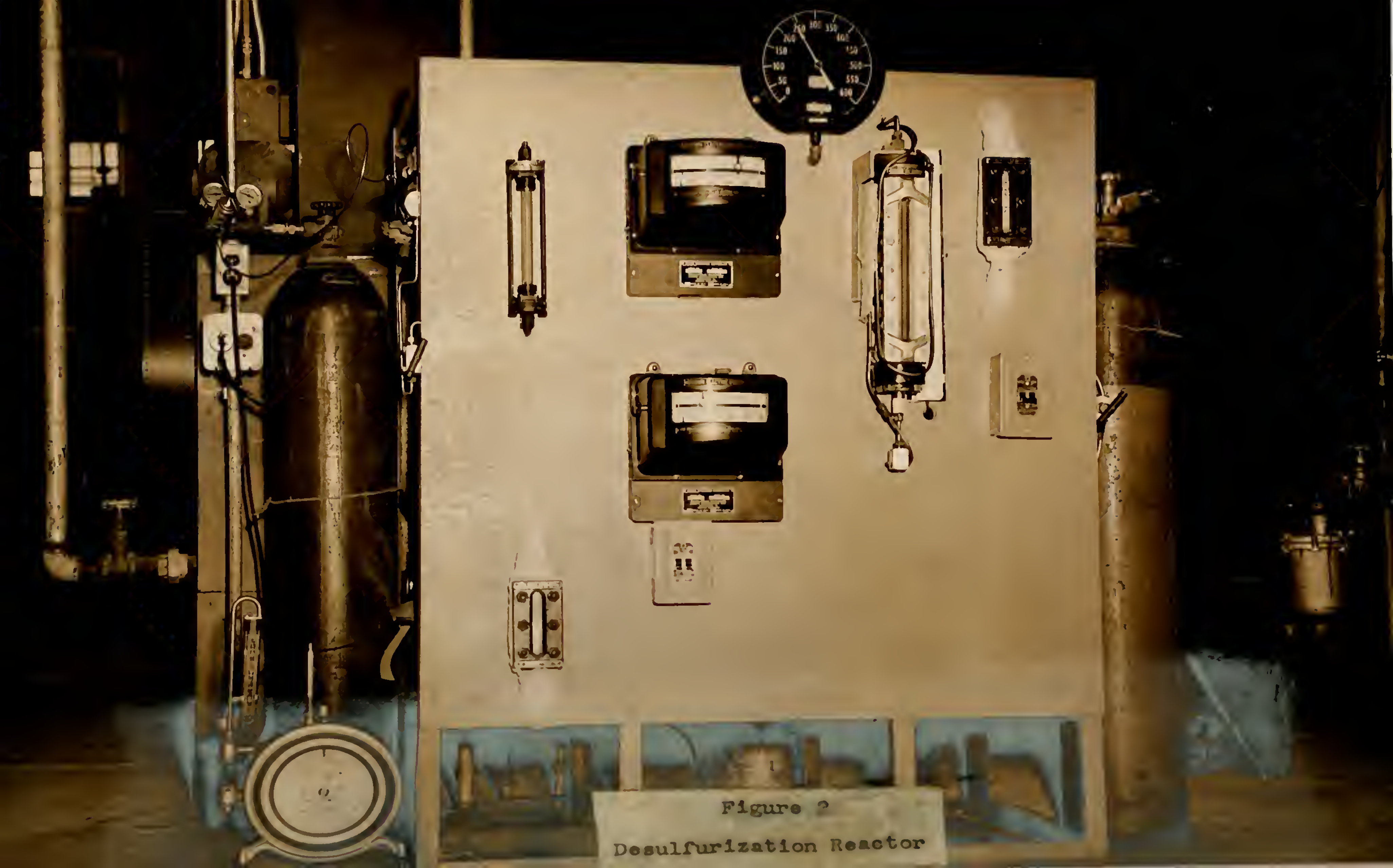
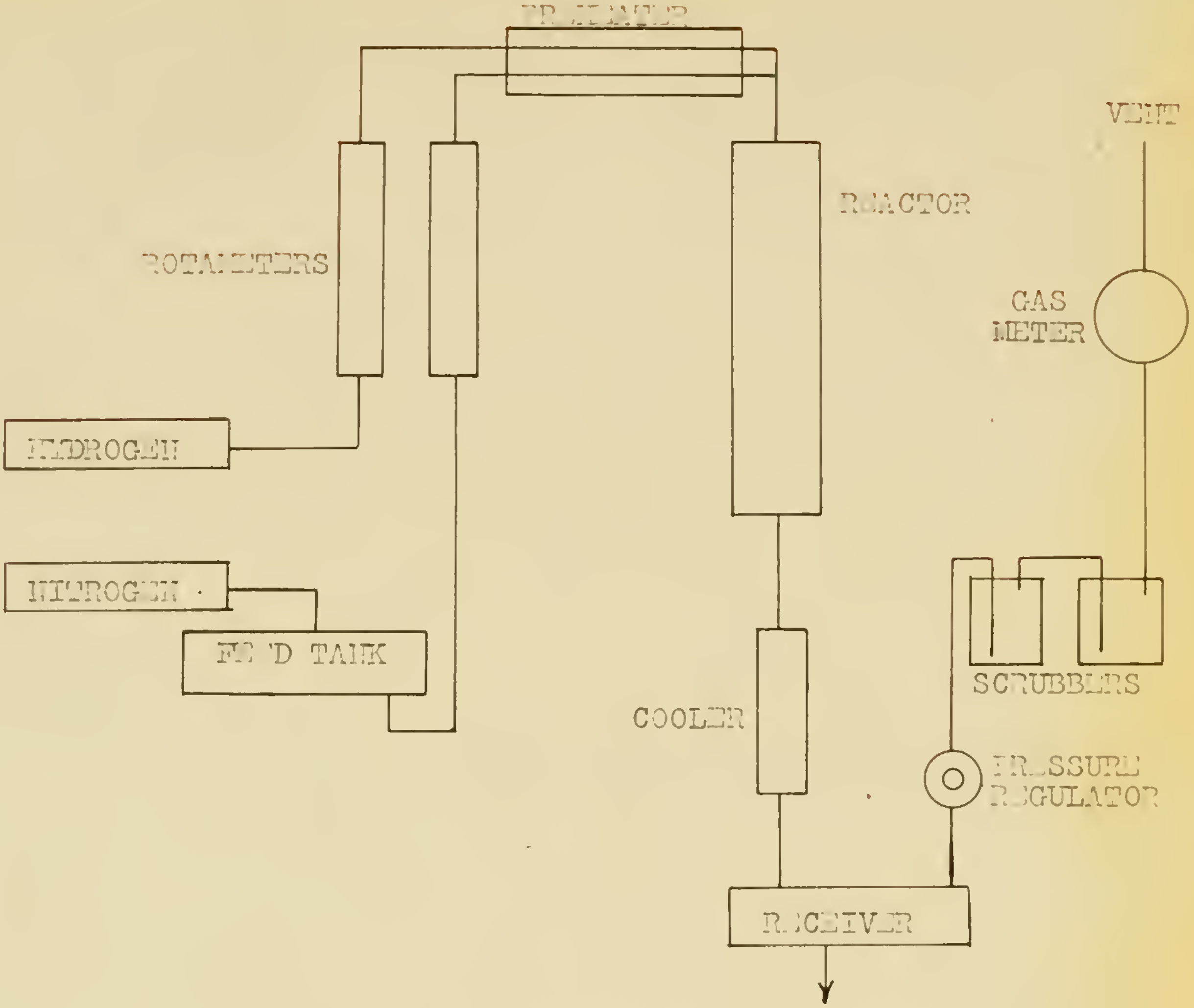


Figure 2

Desulfurization Reactor

Figure 3



FLOW DIAGRAM FOR DESULFURIZER

DRAWN BY: JHG
CHECKED BY:
DATE:
SCALE:

ENGINEERING AND INDUSTRIAL EXPERIMENT STATION
UNIVERSITY OF FLORIDA
GAINESVILLE

DRAWING NUMBER

REVISION

DATE

MATERIAL

TOLERANCES UNLESS OTHERWISE SPECIFIED
DECIMAL
FRACTIONS

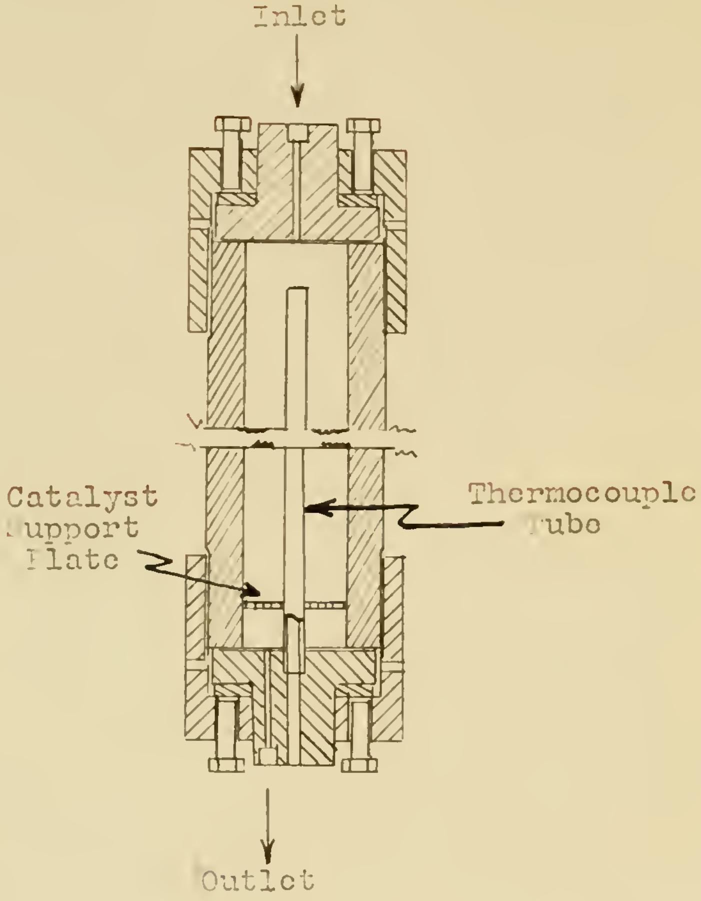
The hydrogen feed rotameter is a standard one-eighth inch Schutte and Koerting rotameter having a maximum operating pressure of 450 pounds per square inch gage.

The feed preheater comprises two stainless steel coils 36 inches long immersed in an oil bath. The hydrocarbon and hydrogen are heated in separate coils in the same oil bath. They are mixed together immediately upon leaving the preheater and the temperature of the combined stream controls the temperature of the oil bath. The oil bath is heated by two 500 watt, 110 volt immersion heaters and its temperature is controlled by a Brown controller.

The reactor is a stainless steel standard Aminco Super-pressure vessel modified to have a removable head on each end and a support plate on each end. The vessel is of the 4-3/8 inch series and has a catalyst capacity of 2200 cubic centimeters. It is constructed of 13 per cent chrome Stainless Steel, Type 410, and has a maximum working pressure of 5600 pounds per square inch at a temperature of 800°F. The vessel is equipped with a heating jacket containing two 800 watt, 220 volt, electric heaters connected as shown in Figure 5. A schematic diagram of the reactor is given in Figure 4.

The cooler is made from a 40 inch length of 0.25 inch stainless steel tubing coiled in a water bath. The water flow is countercurrent to the flow of hydrocarbon.

Figure 4



REACTOR SCHEMATIC

DRAWN BY:
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DATE:
SCALE:

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UNIVERSITY OF FLORIDA
GAINESVILLE

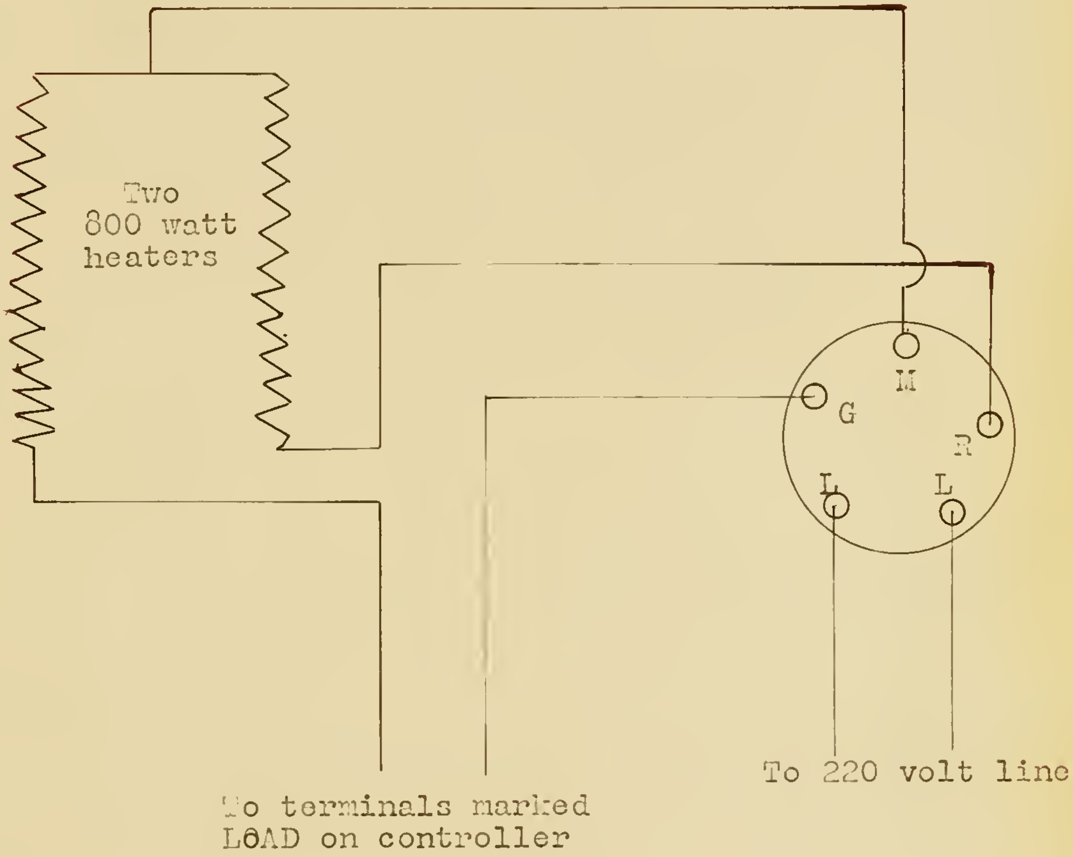
DRAWING NUMBER

REVISION	DATE

MATERIAL
13% chrome stainless steel

TOLERANCES UNLESS OTHERWISE SPECIFIED
DECIMAL FRACTIONS

Figure 5



WIRING DIAGRAM FOR HEATING JACKET WITH CONTROLLER

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UNIVERSITY OF FLORIDA
GAINESVILLE

DRAWING NUMBER

REVISION
DATE

MATERIAL

TOLERANCES UNLESS OTHERWISE SPECIFIED
DECIMAL
FRACTIONS

The scrubbers consist of two 2,000 cubic centimeter Ehrlenmeyer flasks which are partially filled with a cold sodium hydroxide solution. After the liquid is separated from the excess gas in the product tank, the gas is bubbled through the caustic solution which removes the hydrogen sulfide formed during the desulfurization process.

The wet gas meter is standard in design and construction. After the gas passes through the wet gas meter, it is burned in a Fischer type burner adapted for hydrogen burning.

The feed liquid is forced through the system by pressure from a nitrogen cylinder. A standard regulator is used on the cylinder and a pressure approximately five pounds per square inch higher than the reactor pressure is maintained on the feed tank. The rate of feed flow is controlled by a needle valve between the feed tank and the armored rotameter. The feed lines from the feed tank to the preheater are steam traced to prevent solidification of gas oils having high pour points.

The reactor pressure is determined by the pressure setting of the regulator valve on the hydrogen supply tank. This regulator can maintain delivery pressures up to 1,000 pounds per square inch gage.

The back pressure on the system is maintained by a pressure regulator on the product tank. This regulator reduces the pressure from that of operation to approximately fifty pounds per square inch gage. A low pressure reducer then further reduces the pressure to about one pound per square inch gage pressure.

The rate of hydrogen flow is controlled by a needle valve on the exit of the low pressure regulator.

The reactor contains 1,800 cubic centimeters of 7.5 weight per cent cobalt-molybdate supported on Socony alumina bead catalyst.

B. Adsorption Apparatus

The adsorption apparatus shown in Figure 6 was made according to Bureau of Standards specifications (17). The column has a packed section 1250 millimeters in length having a capacity of approximately 160 grams of silica gel. It is supplied with two receivers with capacities of 5.5 milliliters and 10.5 milliliters respectively, graduated to 0.02 milliliters with 0.01 milliliters estimated.

The top of the reservoir of the column is connected by means of a spherical ground joint to a nitrogen cylinder regulator. A cylinder of nitrogen is used to supply the pressure to the column necessary to maintain a product collection rate of seven to thirty milliliters per hour.

The adsorbent used is Davison silica gel with a particle size range from 28 to 200 mesh. It is necessary to use a fresh silica gel charge for each adsorption run.

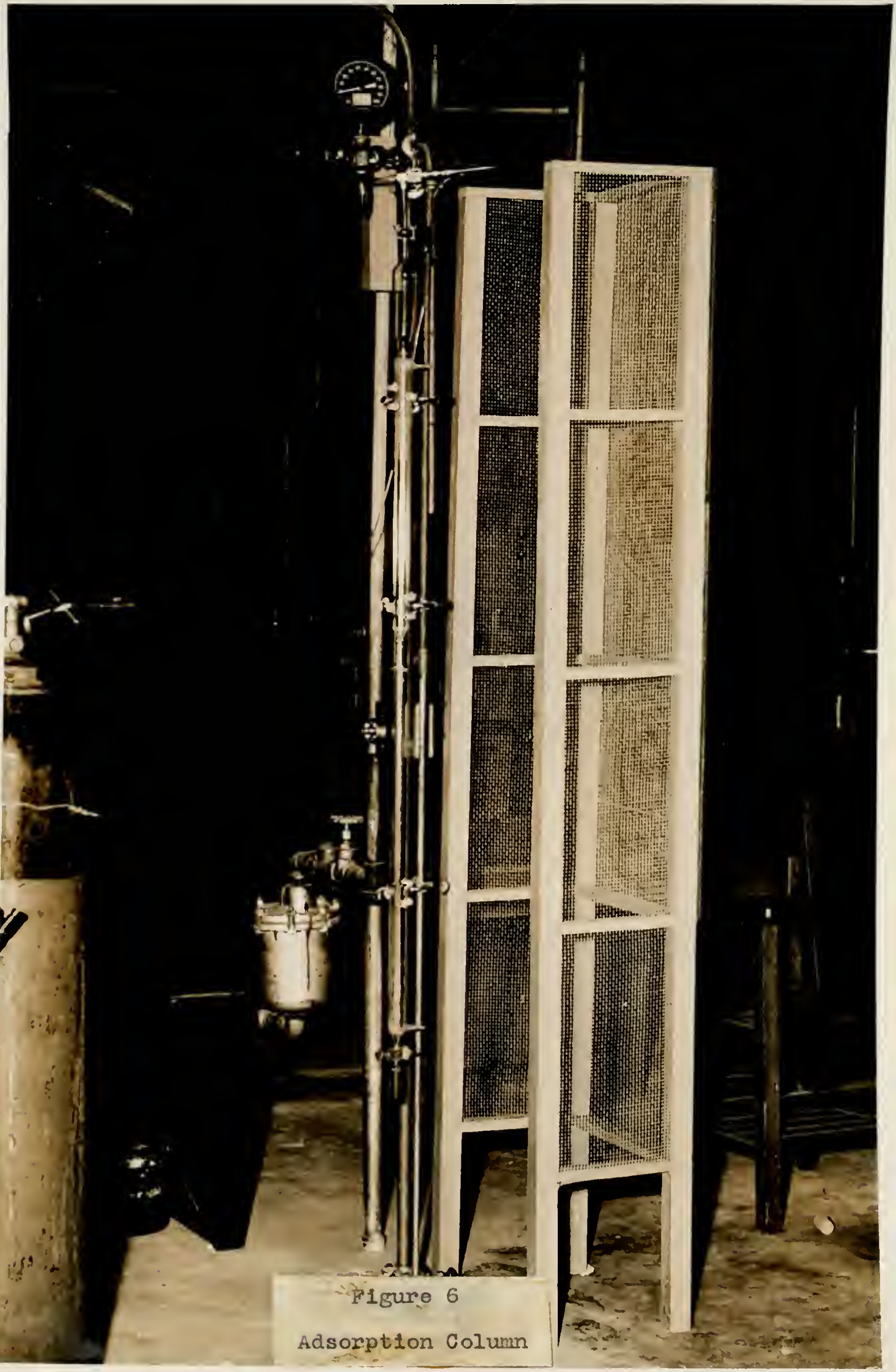


Figure 6

Adsorption Column

V. PROCEDURE

A. Desulfurization Apparatus

All valves on the equipment are closed. Two thousand milliliters of the oil to be desulfurized are charged into the feed tank. The steam to the heating coils is turned on and the oil allowed to reach its equilibrium temperature of approximately 200°F.

The heating units of the reactor and preheater are turned on and the temperature controllers set at 700°F. and 300°F. respectively. After these temperatures are reached the equipment is ready for operation.

One thousand milliliters of a 20 per cent sodium hydroxide solution are put into each of the scrubbing flasks and the water level in the wet gas meter is filled to the correct height.

The pressure regulator on the nitrogen cylinder is adjusted until the pressure on the feed tank is approximately 205 pounds per square inch gage.

The pressure regulator on the hydrogen cylinder is set to deliver hydrogen at 200 pounds per square inch gage pressure and the needle valve between the hydrogen regulator and rotameter is slowly opened fully. The regulator is then adjusted until the reactor pressure gage reads 200 pounds per square inch.

The hydrogen flow rate is adjusted by means of the needle valve on the exit side of the low pressure regulator until a flow rate of about 24 cubic feet per hour is indicated on the rotameter.

The liquid feed rate is set at 900 milliliters per hour by means of the needle valve between the feed tank and armored rotameter.

A wet gas meter reading is taken as the liquid feed is introduced. The temperature, flow rate, pressure and wet gas meter readings are recorded at ten minute intervals.

The hydrogen gas from the wet gas meter is fed to a burner and burned. If necessary the water to the cooler may be turned on. In the case of gas oils having high pour points care must be taken that too low a temperature is not maintained.

Upon the conclusion of the run the hydrogen regulator and liquid feed control valve are closed and the heating units turned off. After the pressure of the system has fallen to atmospheric, the product is removed from the product tank by removing the 0.5 inch pipe plug from the bottom of the tank and the amount of product is measured and recorded.

This procedure is for a liquid hour space velocity (L.H.S.V.) of 0.5, a hydrogen feed rate of 4,000 cubic feet per hour per barrel of product, an average reactor temperature of 650°F., and a reactor pressure of 200 pounds per square inch gage.

B. Adsorption Apparatus

The adsorption column is filled with silica gel and packed by tapping throughout its length with a rubber-covered wooden rod. The packing is continued until the level of the silica gel decreases less than five milliliters in five minutes of packing. Sufficient silica gel should be initially charged so that the final height of the silica gel is about two to five centimeters below the bottom of the reservoir. When filling the column with silica gel a continuous flow should be maintained. Where-ever the flow is stopped, a ring will appear during the adsorption process. While the Bureau of Standards Procedure makes no mention of this effect, it was thought desirable to keep the formation of these rings to a minimum.

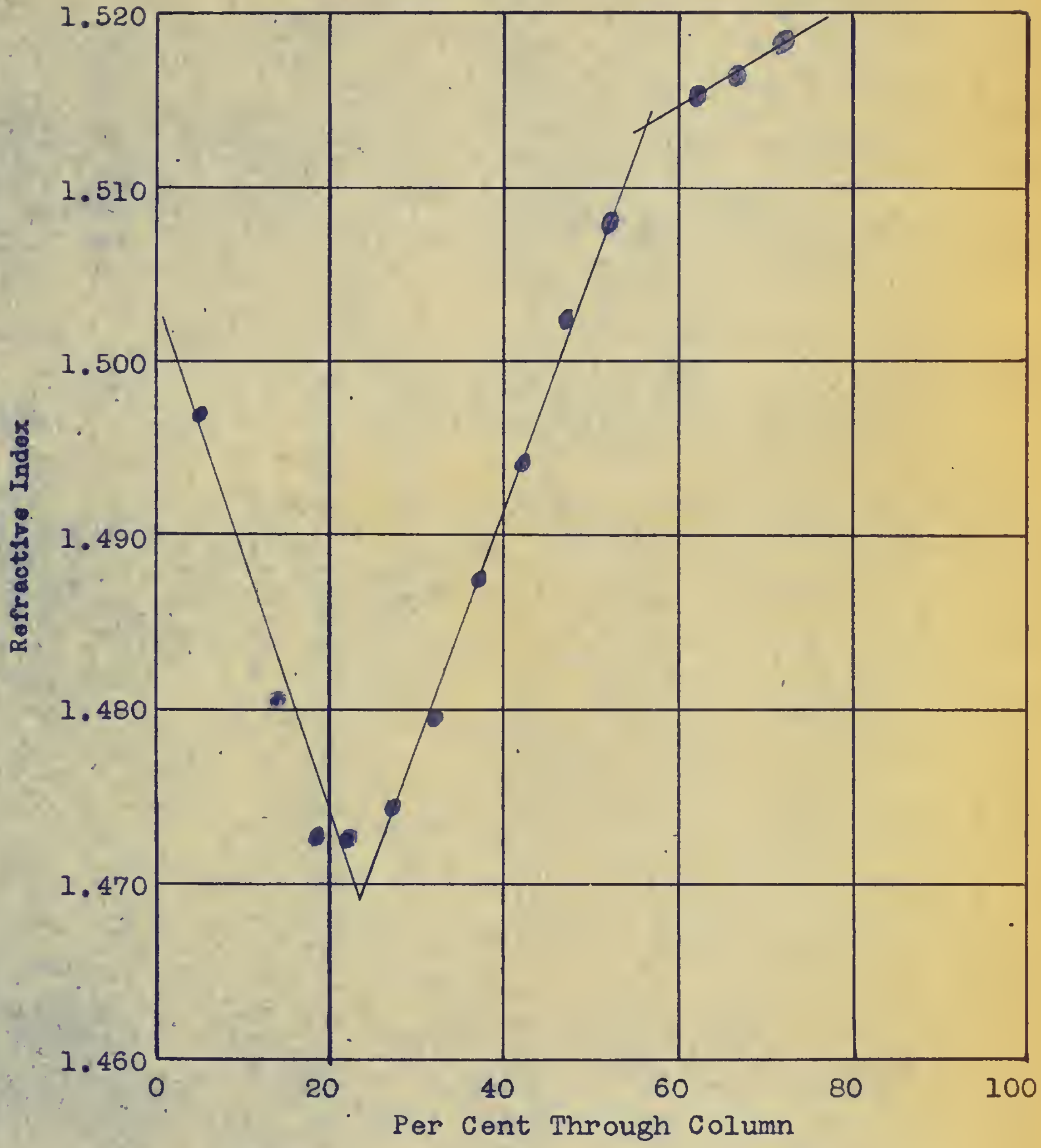
After packing, 100 milliliters of gas oil are introduced into the reservoir, care being taken not to wet the upper portion of the reservoir. Pressure of five to ten pounds per square inch is then applied. After the sample has completely entered the silica gel (about 40 to 60 minutes), the pressure is reduced, the reservoir opened, and a layer of two centimeters of silica gel added. The reservoir is then filled with ethanol or n-hexanol and sufficient pressure applied to give flow rates between ten and thirty milliliters per hour. When a fraction has collected in the receiver, the flow from the adsorption tube is interrupted by closing the stopcock. Forty seconds are allowed for the upper parts of the receiver to drain before the volume is read and an equal interval allowed for drainage after the withdrawal of the bulk of the fraction before the stopcock on the receiver is closed.

Both ethanol and n-hexanol were used as desorbants during the course of the investigation. Ethanol is preferred because it is more easily separated from the hydrocarbon than n-hexanol. It is necessary to completely remove the desorbant before sulfur determinations are made. The ethanol was easily removed by placing the sample in a steam bath for a two hour period. To remove the n-hexanol, it required periods up to 24 hours.

After completely removing the solvent, the volume of hydrocarbon remaining was measured and its refractive index determined. By plotting refractive index versus percent of sample through the adsorption column (percent and ml. were equivalent in this investigation since 100 ml. samples were used), a series of points are obtained. Through these points a series of three straight lines can be drawn, each having a different slope (see Figure 7). The intersections of the center line with each of the other lines denotes the break points between the paraffin and naphthene and naphthene and aromatic fractions. This method is essentially the same as that reported by Mair and Forziati (15).

Figure 7

Typical Refractive Index Plot
Sample S-100-F at 40° C.



Refractive indices were determined at 25°C. except for those samples which were not liquid at this temperature. For samples having pour points above 25°C., the refractive indices were measured at 40°C.

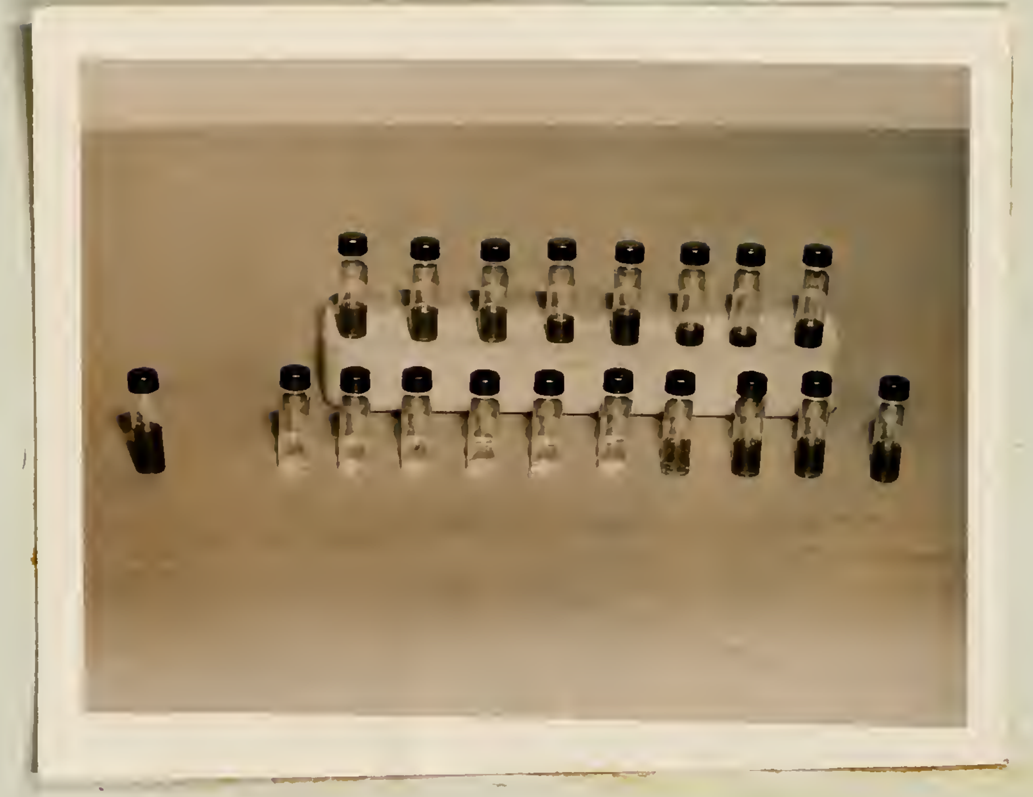
The separation between paraffins and naphthenes was very sharp. In the case of samples containing no sulfur in the paraffin fraction, the point of change could easily be seen. The paraffin fraction was water white and the naphthene fraction deeply colored. The sharp change can be seen in Figure 8. The sample on the extreme left is the original gas oil used as feed to the adsorption column. Because of the dark color of both the naphthene and aromatic portions, the break point could not be determined without the aid of the refractometer.

C. Sulfur Analysis

The sulfur analysis was performed according to the instructions given in American Society for Testing Materials test method E 30-46 T using the equipment manufactured by the Laboratory Equipment Company.

Figure 8

Adsorption Analysis Fractions
Sample G-132



D. Experimental Data

A total of eighteen gas oil samples from nine different crude oils were obtained from oil companies. The crude oils from which the gas oils were commercially separated represented nine separate geographical locations. Because of the different gas oil specifications existing among the oil companies supplying the samples, it was possible to select only one set of samples having the same viscosity and gravity characteristics.

Since the purpose of this investigation was to determine the effect of crude oil source on the catalytic desulfurization mechanism, the samples were selected so as to have all physical characteristics as nearly identical as possible. In addition, one sample having a somewhat different viscosity and gravity was desulfurized to see if any change in desulfurization due to physical properties was indicated.

Also three additional gas oils of widely different physical characteristics were separated into fractions by adsorption to determine the effect of viscosity and gravity on composition and sulfur distribution.

The catalyst used for the desulfurization was selected because more published information was available on catalytic desulfurization using a cobalt-molybdena catalyst than any other kind. The temperature of the desulfurization reaction was shown by Burns, Bradley, and Lee (2) to be rather critical in that temperatures in excess of 750°F. caused excessive cracking of the oil and coking of the catalyst while at temperatures under 600°F. the rate of desulfurization was very low. An average reactor temperature between 600°F. and 700°F. was selected for use in this investigation because it was recommended by the above mentioned authors as being overall the most desirable.

In commercial installations, low-pressure operations are those which are carried out below 250 psig. To operate at pressures in excess of this requires the use of more costly equipment. Because it is desirable to operate at pressures below 250 psig. for this reason and at pressures above 150 psig. in order to obtain a satisfactory reaction velocity, the median pressure of 200 psig was selected for this investigation.

The liquid space velocity and hydrogen rate were chosen to conform with those reported by Huffman (12).

The oils used in this investigation received no special treatment except for washing with a caustic solution to remove free hydrogen sulfide before adsorption and determination of sulfur.

VI. RESULTS

The desulfurization apparatus operated very smoothly and the runs were made at essentially constant conditions. It was found that the hydrogen flow rate could be more easily determined by the wet gas meter than by the hydrogen rotameter. Due to hydrocarbon vapors in the gas the rotor tended to stick in the rotameter tube and the rotor level fluctuated over a wide range. Use of a long pipe cleaner to clean the rotameter tube thoroughly before each run reduced this trouble but did not completely overcome it. Fortunately, once the flow rate was set it remained constant during the run so no operating trouble resulted.

In the case of the Florida oil, sample number S-100-F, the color was so dark that the rotor level could not be determined once the outer portion of the rotameter tube was filled. The flow rate was adjusted while the outer portion was being filled and no further changes were necessary.

The gas flow rates were determined upon the completion of the run by means of the wet gas meter readings and the length of the run in the case of hydrogen and by measuring the feed remaining and the product received in the case of the gas oils.

All runs were made at a liquid hourly space velocity of 0.5, reactor temperature of 650°F., reactor pressure of 200 pounds per square inch gage, and hydrogen feed rate of 4,000 cubic feet per hour per barrel of fresh feed.

The results of the desulfurization runs are shown in Tables 2 to 4. An examination of the data reveals that in every sample, both before and after desulfurization, the per cent sulfur is greatest in the aromatic fraction and least in the paraffin fraction. This is in accordance with the present theories on the subject and tends to substantiate them.

A survey of the amount of sulfur in each of the fractions, both before and after desulfurization, shows that the sulfur contained in the paraffin fractions is, in general, more easily removed than that in the aromatic and naphthene portions. However, all of the sulfur is not removed from the paraffin fraction before desulfurization of the aromatic and naphthenic fractions begins. Desulfurization appears to occur in all fractions simultaneously with the rate of desulfurization being greatest for the paraffinic and least for the aromatic type of sulfur compound.

In every case in which the sulfur content of the paraffin fraction is shown as 0^+ weight per cent, the fraction was water white in color. In the case of sample G-129, the paraffin fraction before desulfurization

Table 2

Tabulation of Data on Desulfurization Feed Stocks

SOURCE*	G-121	G-126	G-129	G-132	G-133	G-137	S-100-F
	W.Texas	Colombia	Kuwait	Fullerton	Fullerton	Venezuela	Florida
Sulfur in Crude*							
Wt. %	1.8	-	2.5	0.46	0.46	0.9	2.66
Vol.of Crude* %	15.0	-	3.4	-	-	2.4	16.3
Sulfur,Wt.%							
Before Desul.	1.692	0.708	2.650	0.506	0.548	0.865	3.360
After Desul.	1.420	0.56	1.80	0.41	0.37	0.61	2.34
Gravity, °API	27.0	25.5	25.4	30.6	28.0	26.2	20.7
Refractive Index	25°C.	25°C.	25°C	25°C.	40°C	25°C	40°C.
Before Desul.	1.4946	1.4959	1.5005	1.4850	1.4878	1.4962	1.5120
After Desul.	1.4920	1.4940	1.4928	1.4850	1.4867	1.4910	1.5023
Pour, °F*	-	-	+65	-	+105	+55	+80
Viscosity							
@ 100°F.,C.S.	14.6	19.0	13.1	12.8	-	10.3	210 SSU
@200°F., C.S.	3.34	3.72	3.72	3.07	6.55	2.69	-
Spec. Gravity							
@ 100°F	0.881	0.888	0.888	0.859	-	0.885	-
@200°F	0.853	0.850	0.855	0.828	0.846	0.849	-
Composition,Vol.%							
Paraffin	15	16	16	20	28	18	27
Naphthene	32	39	33	36	33	30	26
Aromatic	53	45	51	44	39	52	47

Note: * Denotes information determined by company supplying samples.

Table 3

Tabulation of Data on Adsorption Feeds

	G-125	G-128	G-134
Source*	Talco	Kuwait	Fullerton
Sulfur, Wt.%	0.648	1.880	2.210
Gravity, °API	24.7	31.1	25.6
Refractive Index	1.4973(1)	1.4843(2)	1.4900(1)
Vis. @ 100°F.			
c.p.	-	8.15	-
s.s.u.*	-	43.8	-
Vis. @ 210°F.			
s.s.u.	44.5	-	63
c.p.	5.91	-	12.4
Sp.Gr.			
@ 100°F.	-	0.858	-
@ 200°F.	0.854	-	0.856
Composition			
Vol. % P	19	44	46
Vol. % N	35	21	27
Vol. % A	44	34	27

*data determined by company supplying sample.

(1) Refractive Index at 40°C.

(2) Refractive Index at 25°C.

Table 4

Sulfur Distribution in Gas Oils

	Totals	Paraffin		Naphthene		Aromatic	
	Wt.%	Vol.%	Wt.%S	Vol.%	Wt.%S	Vol.%	Wt.%S
G-121	1.68	15.0	0.58	32.0	1.09	53.0	2.32
G-121-P	1.42	15.0	0.39	29.0	0.97	56.0	1.88
G-126	0.71	16.0	0.56	39.0	0.59	45.0	0.74
G-126-P	0.56	17.5	0.24	41.5	0.52	41.0	0.74
G-129	2.65	16.0	1.07	33.0	2.20	51.0	3.36
G-129-P	1.80	18.0	0+	30.5	1.10	51.5	2.74
G-132	0.51	19.5	0+	36.5	0.44	44.0	0.90
G-132-P	0.41	20.0	0+	35.0	0.33	45.0	0.60
G-133	0.55	28.5	0.32	32.7	0.53	38.8	0.64
G-133-P	0.37	27.5	0+	34.7	0.37	37.8	0.62
G-137	0.87	18.5	0.23	30.0	0.64	51.5	1.17
G-137-P	0.61	21.0	0+	28.0	0.36	51.0	0.96
S-100-F	3.36	27.0	2.58	26.0	3.40	47.0	3.77
S-100-F-P	2.34	24.0	1.06	30.5	2.38	45.5	3.04
G-125	0.65	19.0	0.50	35.0	0.64	44.0	0.74
G-128	1.88	44.5	0+	20.5	1.11	34.0	4.71
G-134	2.21	46.0	0.84	27.0	1.62	27.0	3.20

Note: "P" in sample number denotes that
it is a desulfurization product.

contained 1.07 weight per cent sulfur and had a very dark color. After desulfurization, the paraffin sulfur content was negligible and the color was crystal clear or "water white". There were six cases in which the paraffin fraction was "water white" and had 0^+ weight per cent sulfur content. There was no colorless sample having a sulfur content greater than 0^+ weight per cent. These data give confirmation to the work of Rossini, Leslie, Hener, Mair, Willingham and Streiff reported by Sachanen (20). They found that the "water white" portion of a straight-run distillate from a Ponca City crude contained no sulfur. This indicates that when the paraffin fraction is colored, it is due to sulfur compounds present and that a lack of color indicates a sulfur-free fraction.

In Figure 9, the weight per cent sulfur after desulfurization is plotted against weight per cent original sulfur. A straight line passing through the origin can be drawn through these points indicating that the source of the gas oil is not a factor in its degree of desulfurization by low pressure hydrogenation using a cobalt-molybdena catalyst. The line drawn between the points has a slope of 0.725.

The weight per cent sulfur after desulfurization is plotted versus weight per cent original sulfur in Figure 10 for each of the gas oil fractions. In every case a straight line results, but the slope of the line is different for

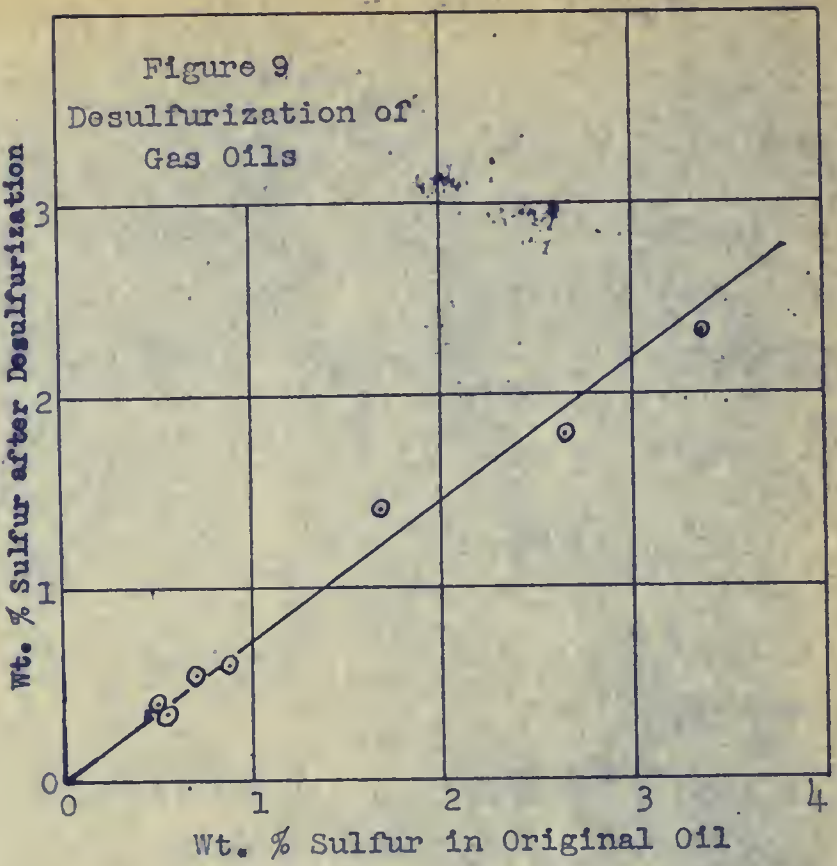


Figure 9
Desulfurization of Gas Oils

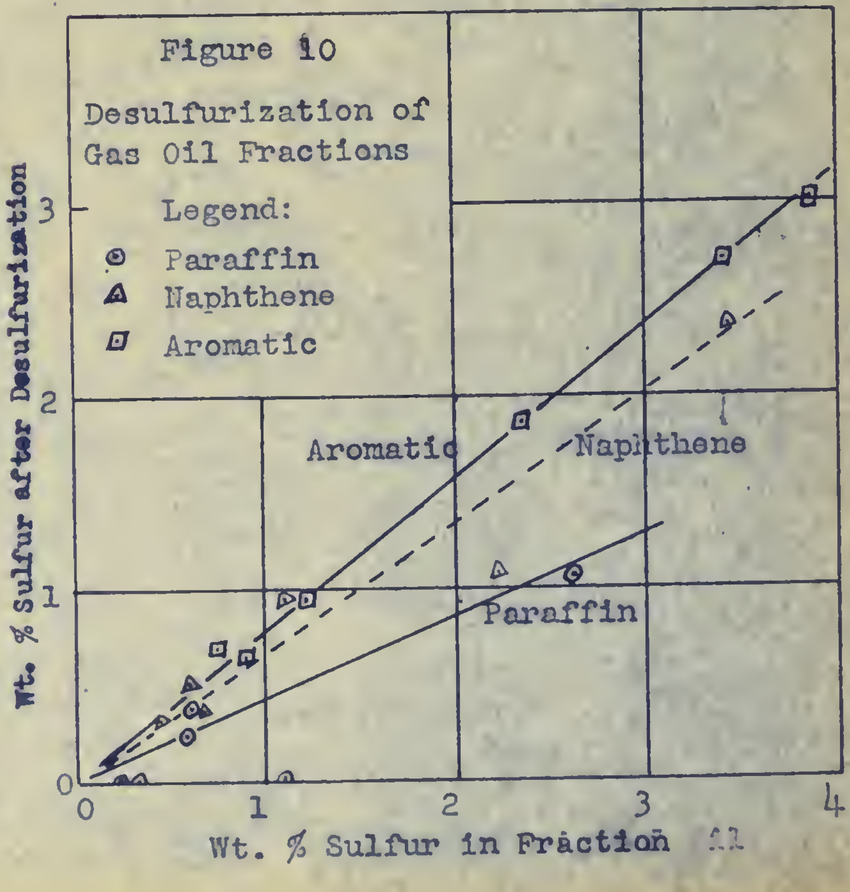


Figure 10
Desulfurization of Gas Oil Fractions

each fraction. For the paraffin fraction the line has a slope of 0.80, for the naphthene fraction a slope of 0.68, and for the aromatic fraction a slope of 0.43. Perhaps the only significance that can be attributed to these curves is that the greater the slope the more difficult the sulfur is to remove.

Graphs of the type used by Hughes, Stine, and Faris (13) are given in Figures 11 to 20 for each of the gas oils used. A plot of sulfur content versus per cent through the adsorption column is shown. This gives a graphical representation of where the sulfur in each fraction is located and its degree of removal.

The samples of oils from the various sources used in the desulfurization runs were, in general, selected with the same viscosity and specific gravity. The object of this type of selection was to have oils from different sources having similar physical properties. The oils selected for desulfurization were from West Texas, Kuwait, Colombia, Venezuela and Fullerton fields. Two oils having gravities very close together but greatly different viscosities were selected from the Fullerton gas oils to determine the effect of viscosity on sulfur distribution. In addition, a third Fullerton sample with a different gravity and viscosity was analyzed to determine the variation in sulfur composition among a range of oils

Figure 11
Distribution of Sulfur in Sample G-121
(Gas Oil from West Texas Crude)

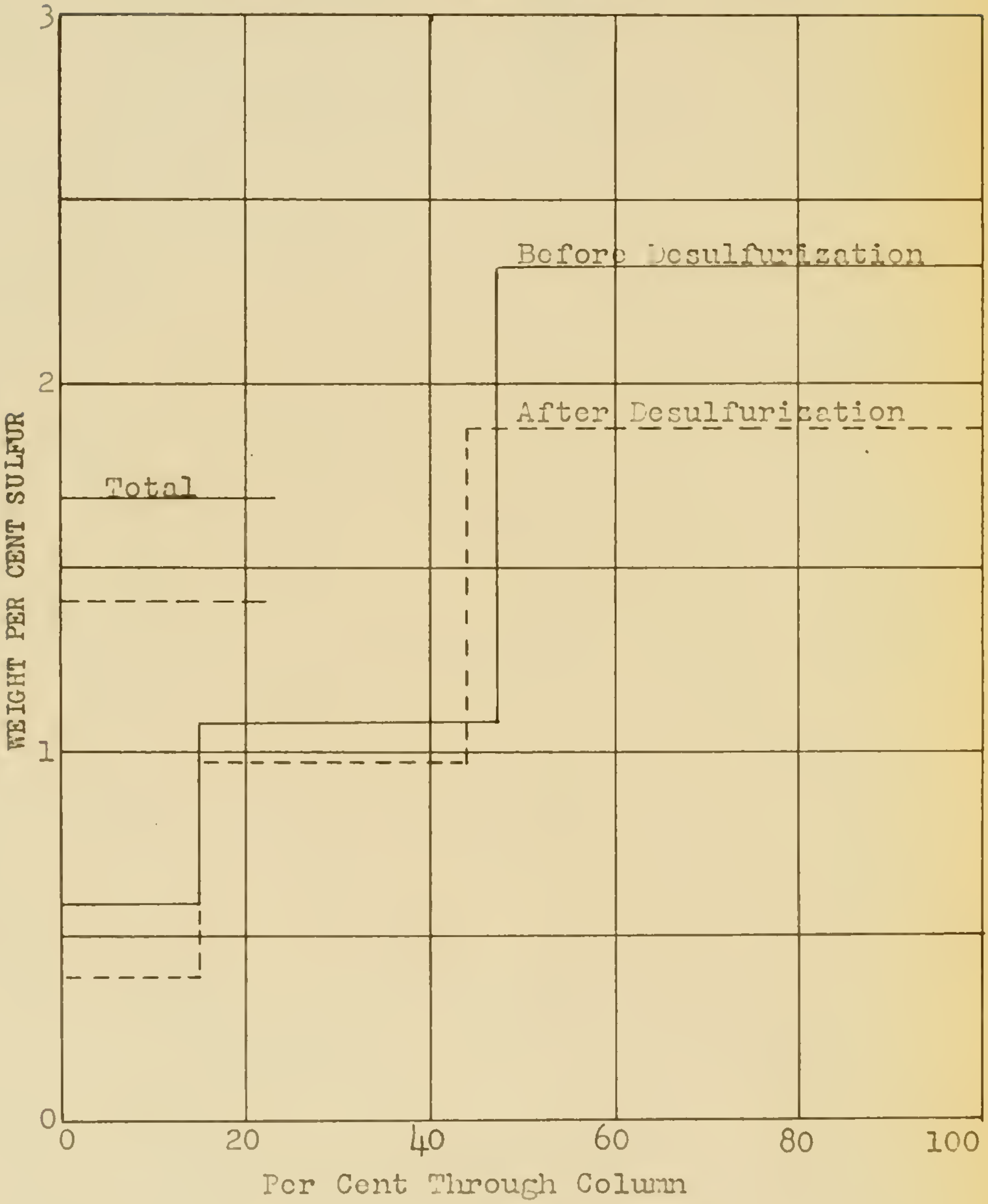


Figure 12 . Sulfur Distribution in Sample G-126

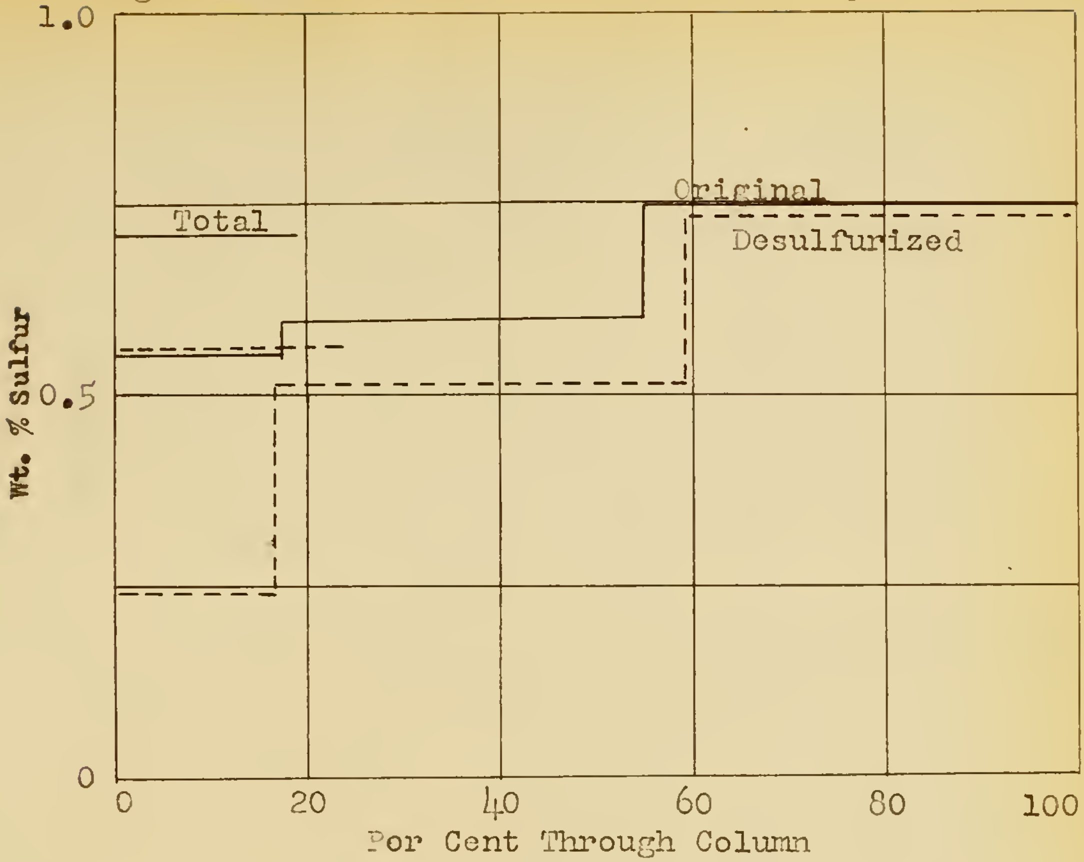


Figure 13. Sulfur Distribution in Sample G-132

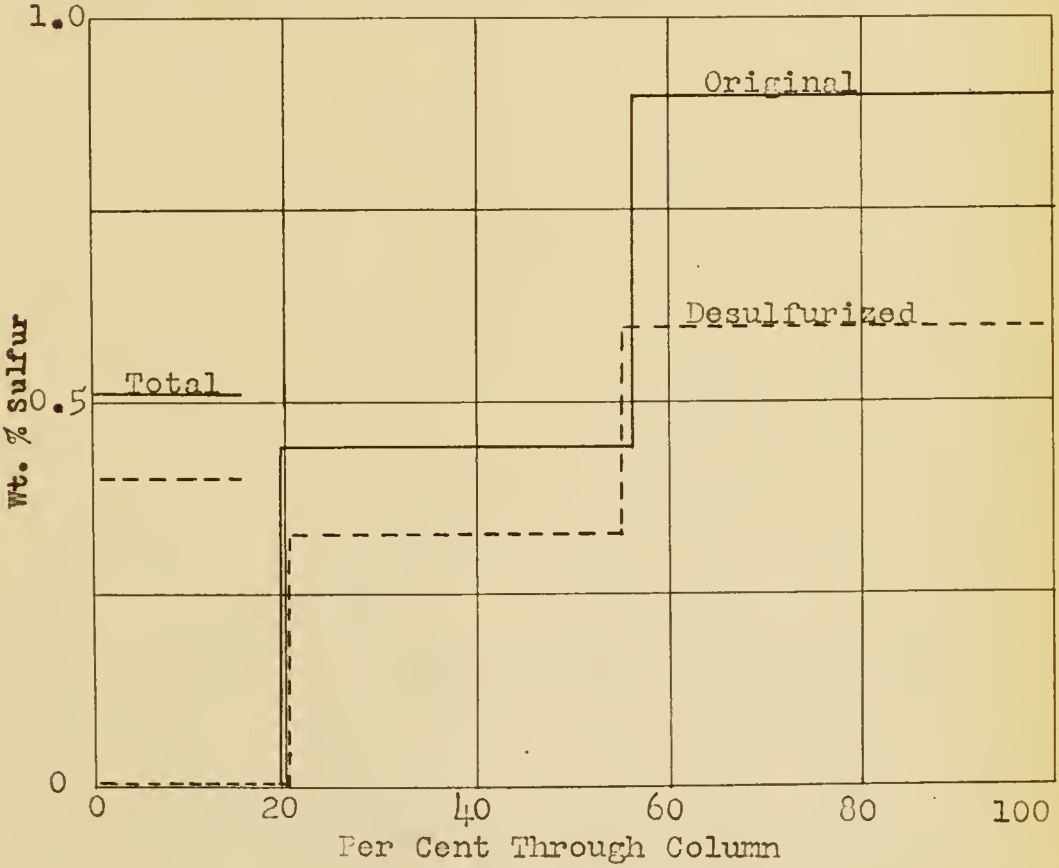


Figure 14

Sulfur Distribution in Sample G-129

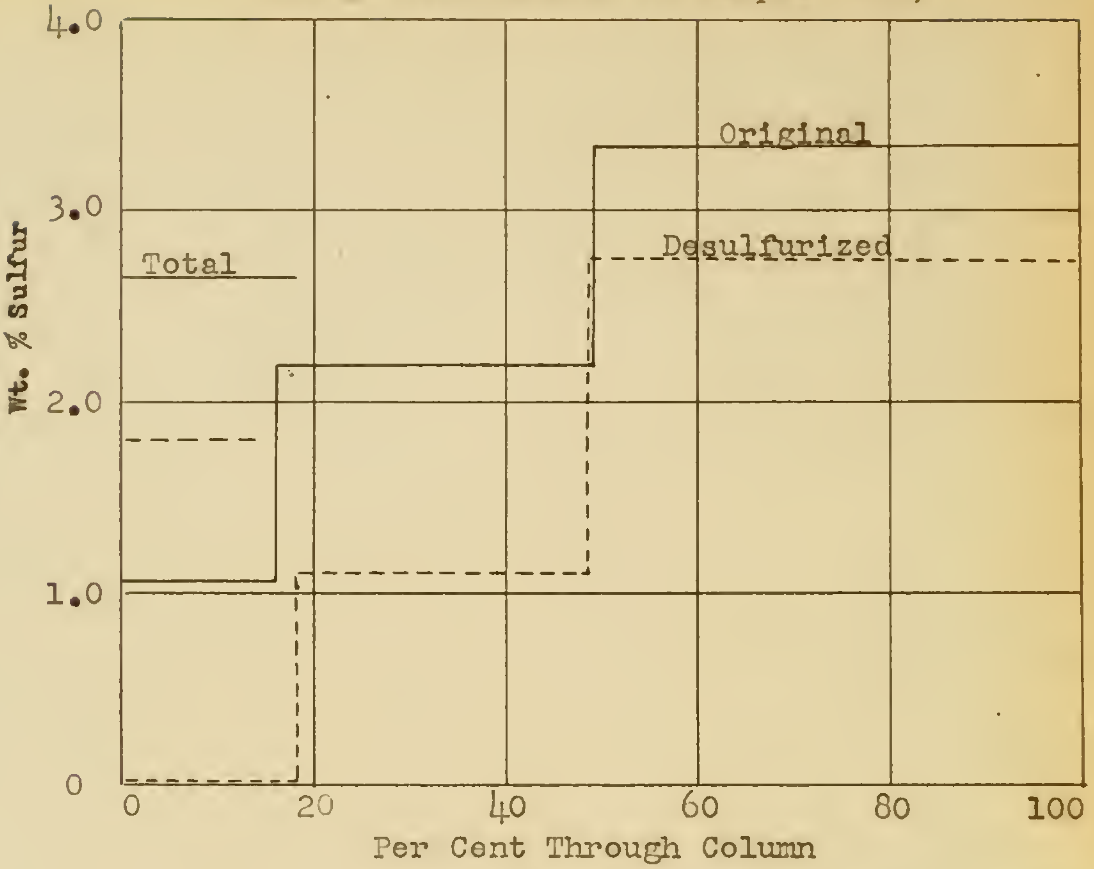


Figure 15

Sulfur Distribution in Sample G-133

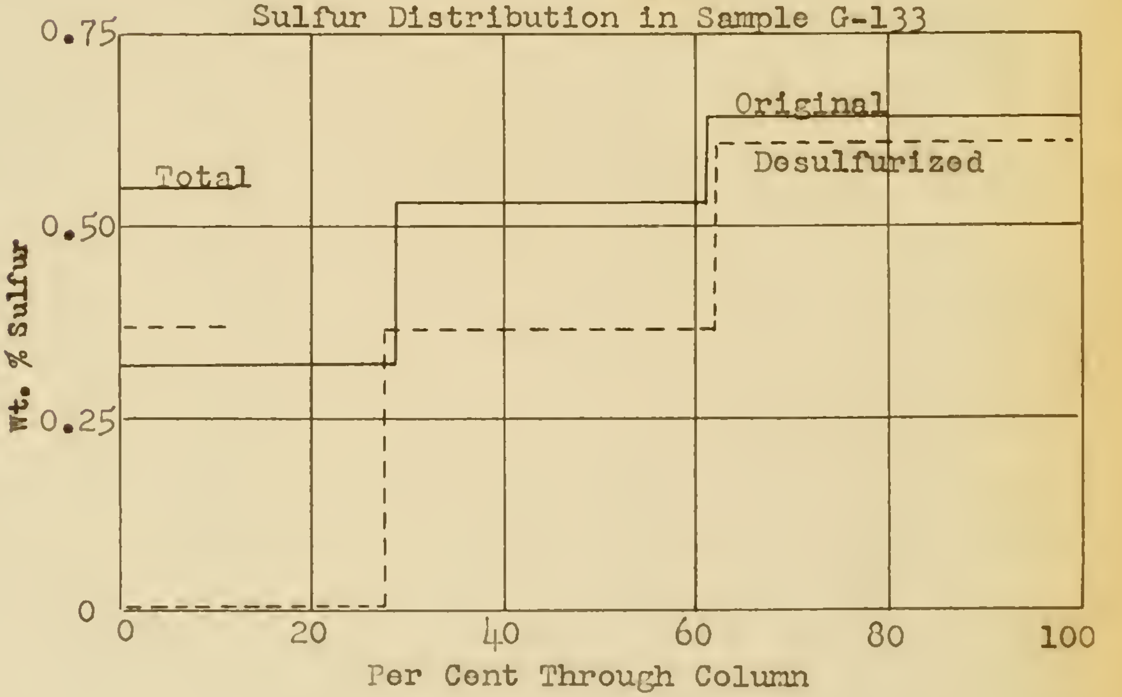


Figure 16. Sulfur Distribution in Sample G-128

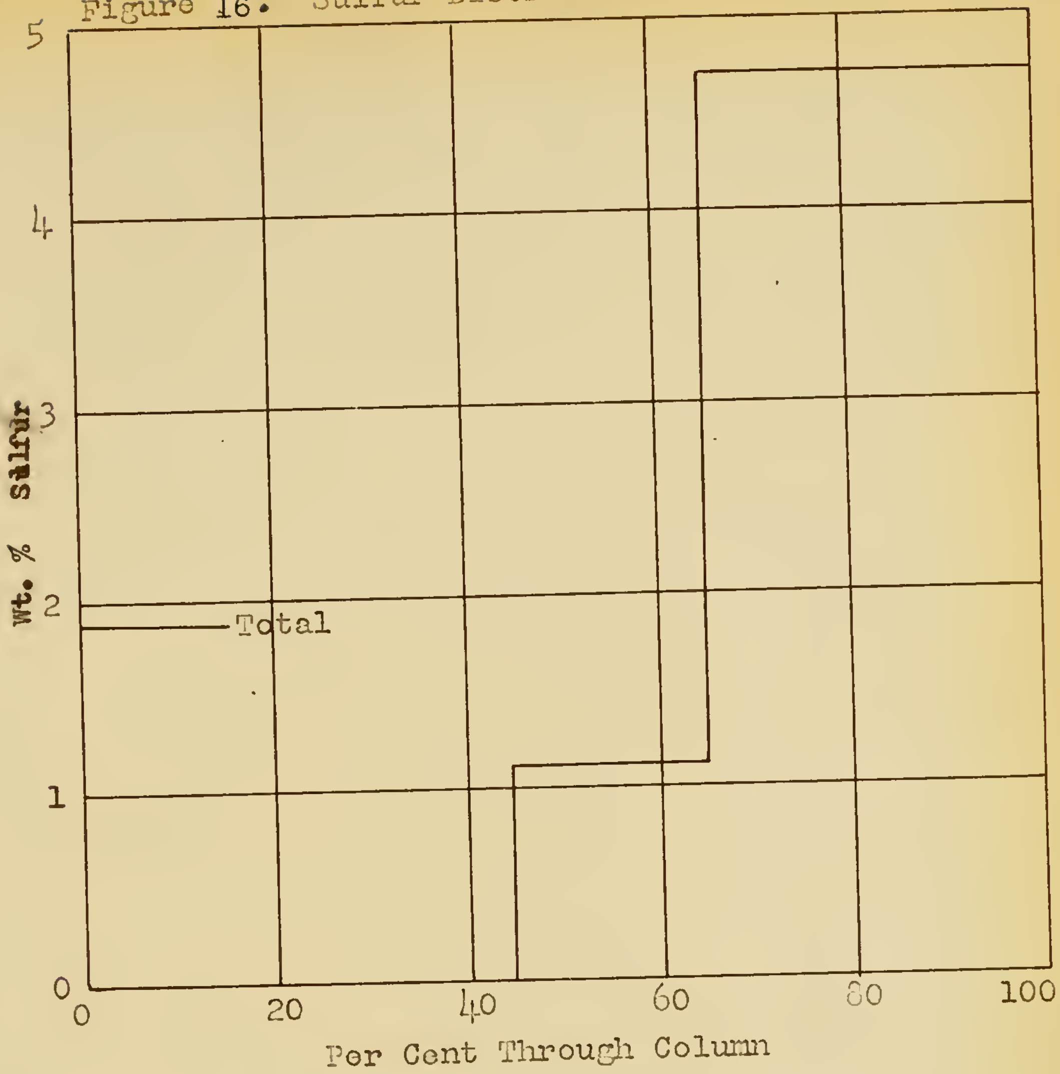


Figure 17. Sulfur Distribution in Sample G-137

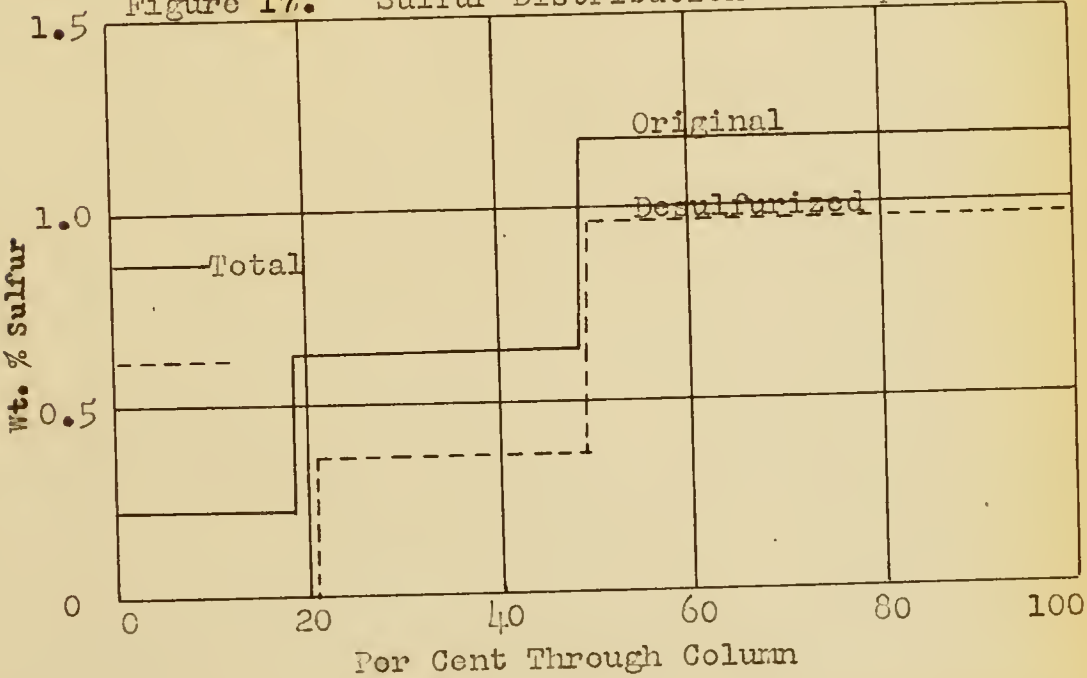


Figure 18

Sulfur Distribution in Sample S-100-F
(Gas Oil from Florida Crude)

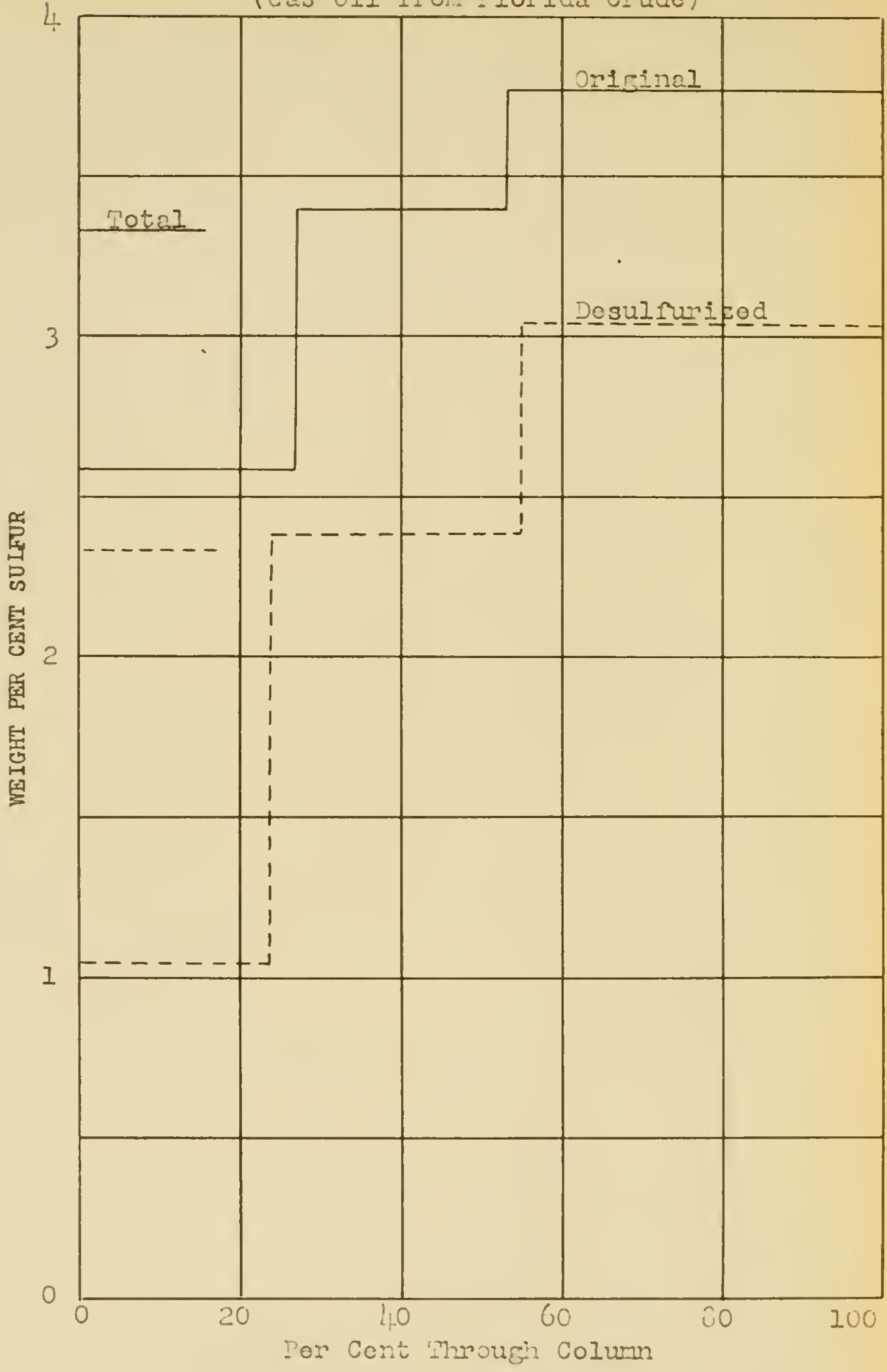


Figure 19

Sulfur Distribution in Sample G-134
(Gas Oil from Fullerton Crude)

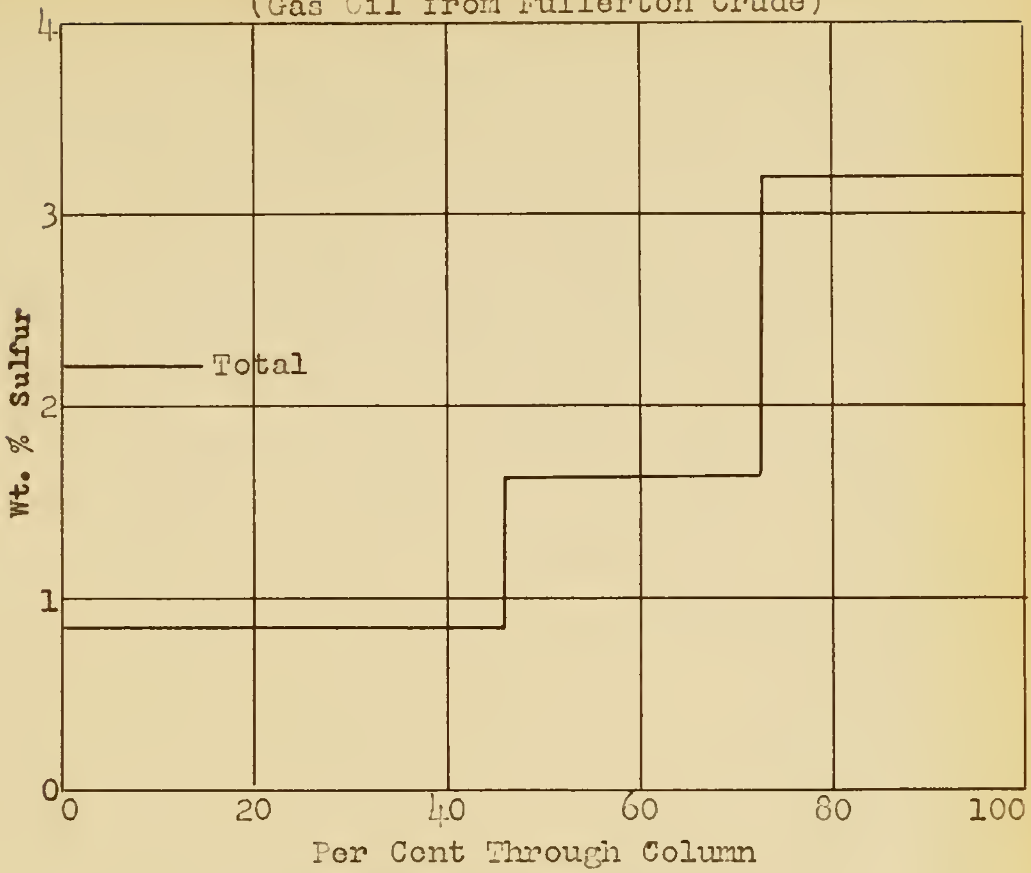
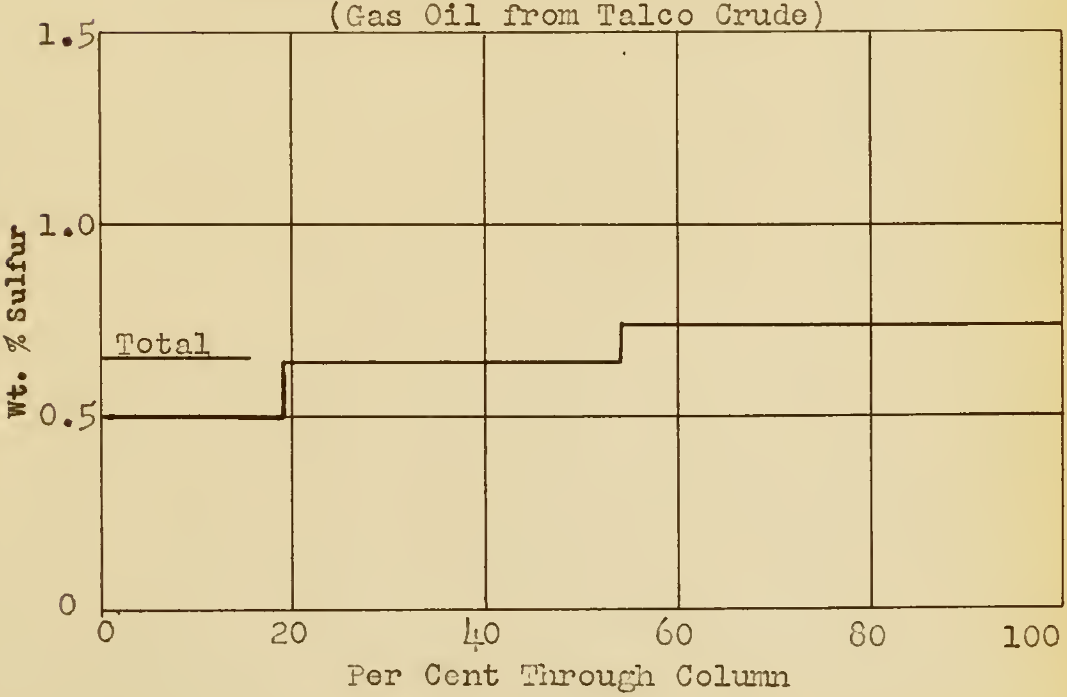


Figure 20

Sulfur Distribution in Sample G-125
(Gas Oil from Talco Crude)



from the same field. A heavy Talco and light Kuwait were also analyzed to determine the sulfur distribution.

It was found that for all of the oils with similar gravities and viscosities the composition, within reasonable limits, was the same. For example, the weight per cent paraffins was in the range 15 to 20 per cent, naphthenes from 30 to 36 per cent, and aromatics from 44 to 53 per cent. In the case of the three samples run on Fullerton gas oils a plot of viscosity in centistokes versus weight per cent gave straight lines for each of the fractions (Figure 21).

For two of the virgin gas oils analyzed there was no appreciable sulfur in the paraffin fraction. In every other case, the higher the specific gravity of the gas oil from a given source the greater the weight per cent sulfur in all the fractions. In the case of the oils having no sulfur in the paraffin fractions, the densest of the two oils from the same source had less sulfur in the aromatic fraction even though the total sulfur content of the heavier gas oil was higher. There is no apparent explanation for this but it may be due to an effect the sulfur content of a molecule has on its adsorptivity. The determination of this effect has been made the purpose of another investigation.

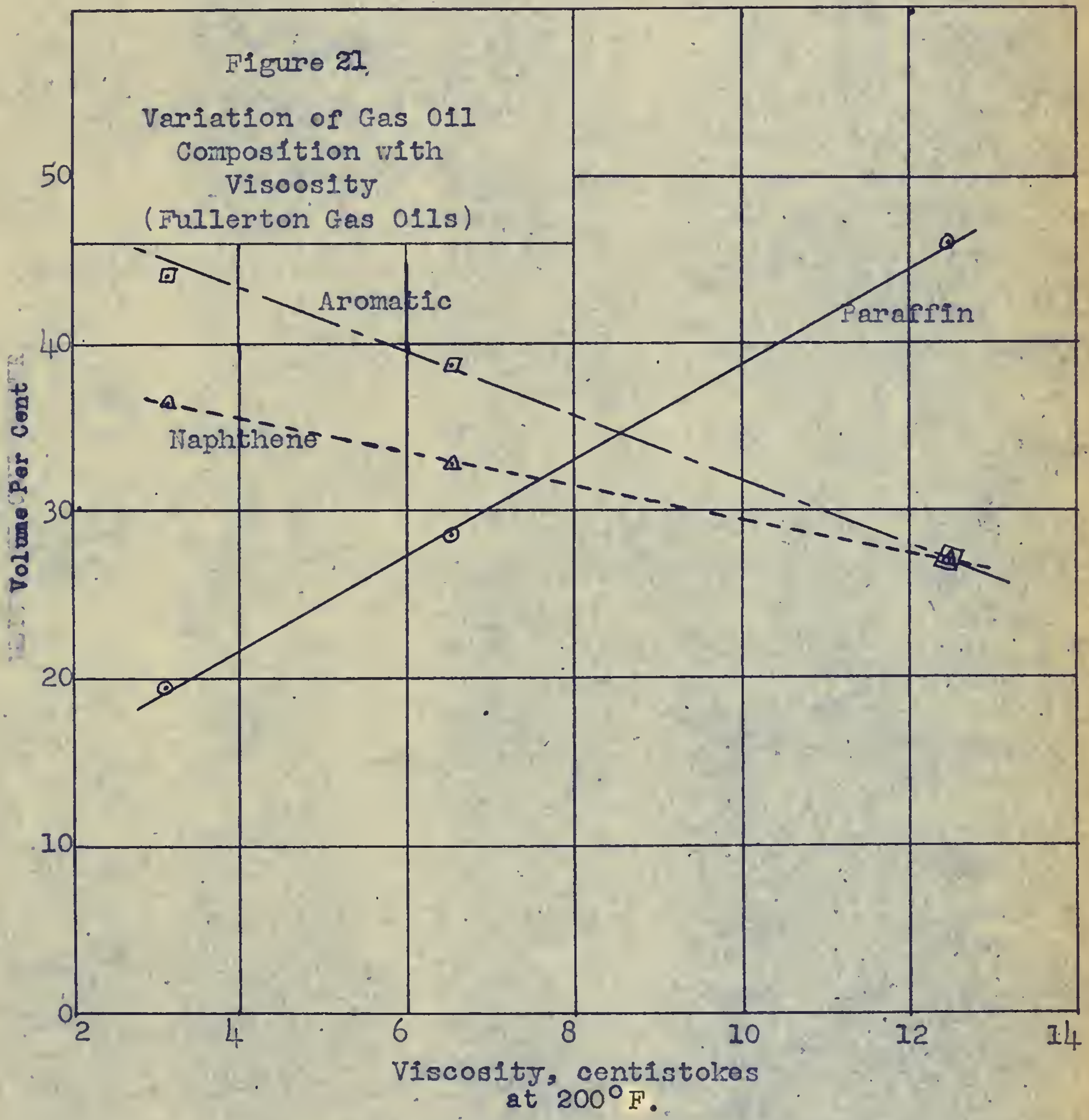
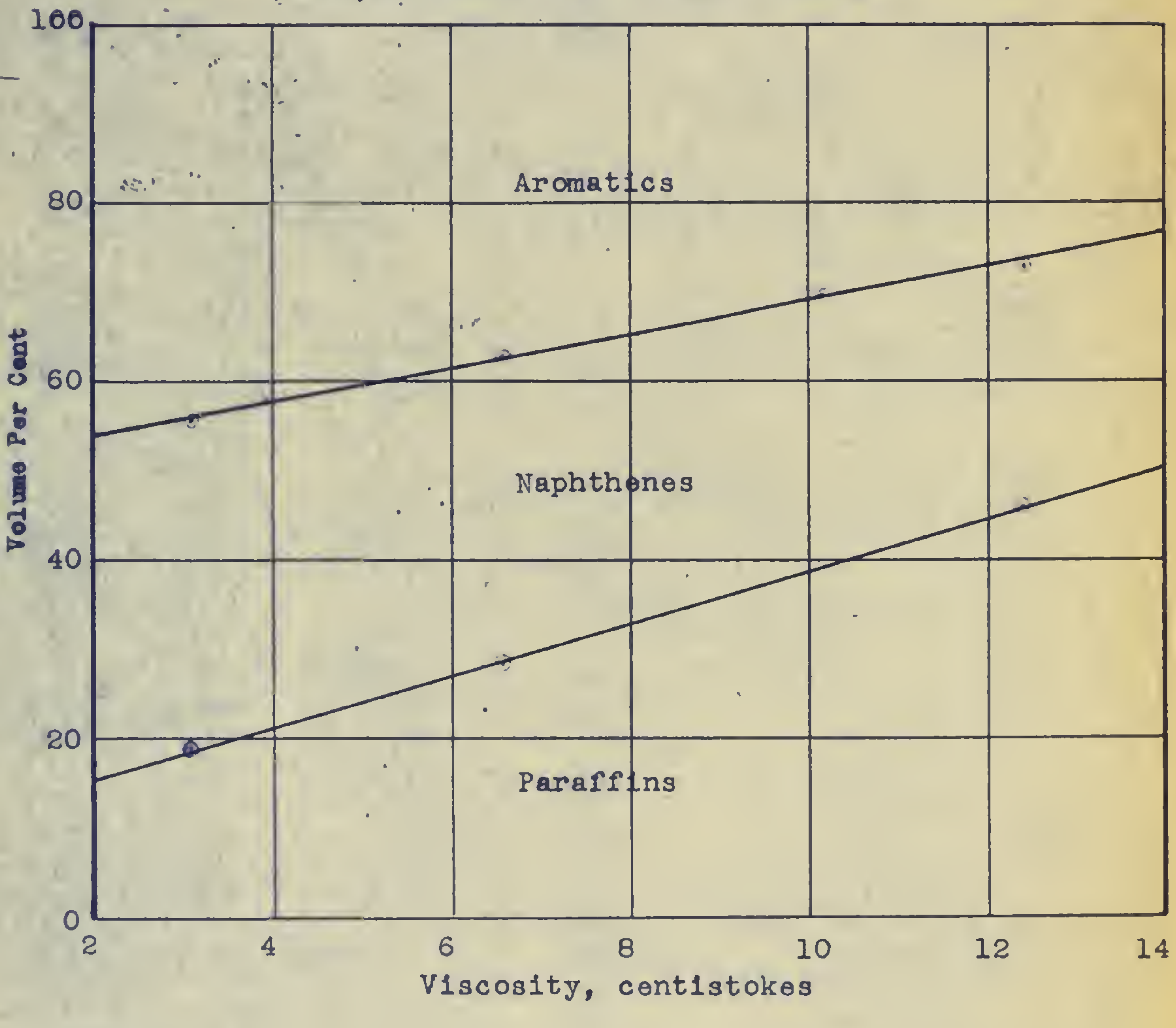


Figure 21

Variation of Gas Oil Composition with Viscosity (Fullerton Gas Oils)

Figure 22
Variation of Gas Oil Composition with Viscosity
Fullerton Gas Oils at 200°F.



VI. CONCLUSIONS

Based on the data obtained during this investigation, the following conclusions are drawn:

A. The aromatic portion of the gas oils has the highest sulfur content and the paraffin fraction the lowest sulfur content.

B. The sulfur in the paraffin fraction is the most easily removed.

C. Sulfur content reduction occurs in all three fractions simultaneously.

D. The complete removal of sulfur gives a "water-white" paraffin fraction.

E. The source of the crude is not a factor in the low pressure desulfurization of a gas oil when a cobalt-molybdate catalyst is used.

F. Gas oils having the same viscosity and specific gravity contain approximately the same amount of paraffins, naphthenes, and aromatics. This indicates that viscosity and gravity delineate composition.

G. In the case of gas oils from a Fullerton crude, the amount of each of the molecular types present (i.e. - paraffin, naphthene, and aromatic) varies linearly with the viscosity at 200°F. in centistokes.

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IX. APPENDIX

Table 5-A

Tabulation of Desulfurization Data

	Time Min.	Feed Rotameter	Reactor Inlet, °F.	Reactor psig.	Wet Gas Meter Cu.Ft.	°F.	in.H_2O
G-121	0	240	650	200	340.0	80	0.2
	10	245	500	200	356.0	80	0.2
Rotor #3	20	245	460	200	369.0	80	0.9
0.2 gm	30	240	480	200	373.3	80	0.9
	40	235	490	200	377.8	80	0.9
	50	235	495	200	381.9	80	0.9
	60	245	480	200	386.0	80	0.9
	70	235	490	200	390.0	80	0.9
	80	246	480	200	393.9	80	0.9
	90	249	490	200	397.8	78	0.9
	100	243	490	200	401.7	78	0.9
	110	243	495	200	405.5	78	0.9
	120	249	495	200	410.4	78	0.9
G-126	0	151	700	200	499.6	81	1.6
	10	155	590	200	505.3	81	1.7
Rotor #2	20	150	550	200	511.2	81	1.7
0.36 gm	30	151	545	200	516.5	81	1.7
	40	150	550	200	521.2	81	1.3
	50	149	550	200	525.5	81	1.2
	60	150	550	200	530.4	81	1.5
	70	143	560	200	535.4	81	1.4
	80	157	555	200	540.4	81	1.4
	90	148	560	200	545.3	81	1.4
	100	148	560	200	550.2	81	1.4
	110	156	560	200	554.9	81	1.4
	120	149	555	200	559.3	81	1.4

Table 5-B

Tabulation of Desulfurization Data

	Time Min.	Feed Rotameter	Reactor Inlet, °F.	Reactor psig.	Wet Gas Meter		
					Cu.Ft.	°F.	in.H_2O
G-129	0	250	700	200	424.4	75	1.7
	10	250	600	200	427.6	75	0.9
Rotor #3	20	230	550	200	431.0	75	1.0
0.2 gm	30	245	540	200	434.8	75	0.8
	40	230	550	200	439.6	75	1.5
	50	240	540	200	445.0	75	1.3
	60	238	550	200	449.8	75	1.1
	70	242	550	200	453.6	75	1.2
	80	242	550	200	457.9	76	1.1
	90	242	560	200	461.9	76	1.4
	100	239	560	200	466.6	76	1.1
	110	242	560	200	470.6	76	1.4
	120	245	560	200	475.5	76	1.3
G-132	0	150	700	200	573.5	81	1.2
	10	158	580	200	576.8	81	1.2
Rotor #2	20	157	545	200	580.4	81	1.3
0.36 gm	30	140	540	200	586.0	81	1.4
	40	139	545	200	591.4	81	1.4
	50	145	545	200	596.9	81	1.4
	60	144	545	200	602.3	81	1.4
	70	135	550	200	607.9	81	1.5
	80	135	560	200	613.7	81	1.5
	90	141	560	200	618.3	81	1.2
	100	144	560	200	622.5	81	1.1
	110	140	560	200	626.6	81	1.1
	120	137	570	200	630.7	81	1.1

Table 5-C

Tabulation of Desulfurization Data

	Time Min.	Feed Rotameter	Reactor Inlet, $^{\circ}F$.	Reactor psig.	Wet Gas Meter		
					Cu.Ft.	$^{\circ}F$.	in.H_2O
G-133	0	170	700	200	714.5	82	1.4
	10	174	620	200	716.8	82	0.6
Rotor #2	20	165	580	200	722.4	82	1.4
0.36 gm	30	127	600	200	728.4	82	1.4
	40	155	590	200	734.7	82	1.8
	50	149	605	200	741.2	82	2.0
	60	155	610	200	747.0	82	1.6
	70	151	610	200	752.6	82	1.5
	80	149	610	200	758.2	82	1.5
	90	154	610	200	763.8	82	1.5
	100	156	605	200	769.5	82	1.5
	110	154	610	200	775.6	82	1.6
	120	150	610	200	780.4	82	1.6
G-137	0	78	700	200	641.2	82	1.2
	10	64	640	200	644.8	82	0.9
Rotor #2	20	70	630	200	649.7	82	1.4
0.36 gm	30	80	630	200	654.9	82	1.4
	40	75	610	200	660.2	82	1.4
	50	75	620	200	665.5	82	1.4
	60	89	610	200	670.7	82	1.4
	70	76	610	200	675.9	82	1.4
	80	86	610	200	681.0	82	1.4
	90	71	610	200	686.0	82	1.4
	100	80	605	200	690.8	82	1.4
	110	83	590	200	695.8	82	1.4
	120	79	550	200	700.8	82	1.4

Table 5-D

Tabulation of Desulfurization Data

	Time Min.	Feed Rotameter	Reactor Inlet, °F.	Reactor psig.	Wet Gas Meter		
					Cu.Ft.	°F.	In.H_2O
S-100-F	0	220	700	200	892.3	67	0.9
	10	220	570	200	898.5	67	1.7
Rotor #2	20	-	570	200	904.6	67	1.7
0.36 gm	30	-	570	200	910.6	67	1.7
	40	-	560	200	916.3	67	1.5
	50	-	570	200	922.2	67	1.7
	60	-	560	200	927.5	67	1.0

Table 6-A

Tabulation of Adsorption Analyses Results

Sample No.	G-121		G-121-P		G-126		G-126-P	
	Ml.	R.I.	Ml.	R.I.	Ml.	R.I.	Ml.	R.I.
1	5.22	1.491	4.92	1.483	5.08	1.500	4.86	1.477
2	5.30	1.480	4.90	1.471	5.30	1.497	5.12	1.474
3	5.77	1.474	5.08	1.467	5.24	1.495	4.64	1.472
4	5.20	1.473	5.00	1.467	5.18	1.494	4.98	1.473
5	5.29	1.475	5.24	1.470	5.24	1.493	5.04	1.474
6	5.12	1.487	5.00	1.476	5.16	1.493	5.12	1.478
7	5.18	1.493	5.28	1.482	5.08	1.493	5.04	1.483
8	5.16	1.497	5.04	1.486	5.30	1.493	6.10	1.488
9	5.70	1.496	5.12	1.491	5.20	1.493	5.50	1.493
10	4.98	1.496	5.16	1.493	5.04	1.493	5.15	1.499
11	5.22	1.494	5.00	1.495	5.08	1.494	5.13	1.504
12	4.20	1.497	5.46	1.499	5.02	1.495	5.22	1.507
13	3.40	1.500	4.98	1.500	5.32	1.497	6.02	1.507
14	3.2	1.502	5.50	1.502	5.48	1.500	5.16	1.511
15	3.3	1.503	4.96	1.506	5.28	1.500	5.14	1.510
16	4.9	1.506	2.6	1.509	3.4	1.500	5.18	1.508
17	3.4	1.512	1.8	1.513	4.4	1.504	2.10	1.508
18	3.1	1.514	2.8	1.507	2.5	1.504	1.3	1.508
19	2.3	1.517	2.3	1.508	9.4	1.504	1.8	1.508
20	2.2	1.516	7.6	1.502			4.8	1.508
21	1.6	1.518	2.8	1.498			4.7	1.508
22	9.7	1.517						
Total	99.44		97.34		97.7		98.10	

Note: R.I. @ 20°C.

Table 6-B

Tabulation of Adsorption Analyses Results

Sample No.	G-129		G-129-P		G-132		G-132-P	
	Ml.	R.I.	Ml.	R.I.	Ml.	R.I.	Ml.	R.I.
1	4.1	1.494	4.96	1.4528	5.12	1.4590	5.00	1.4602
2	5.0	1.484	5.00	1.4501	5.24	1.4579	5.16	1.4585
3	4.8	1.478	5.07	1.4501	5.00	1.4574	4.98	1.4581
4	4.9	1.482	5.48	1.4516	4.93	1.4574	4.65	1.4602
5	5.0	1.488	5.05	1.4530	5.08	1.4574	5.01	1.4633
6	5.4	1.491	5.14	1.4588	5.14	1.4574	4.85	1.4679
7	5.1	1.493	5.15	1.4654	4.87	1.4600	5.18	1.4722
8	5.4	1.496	5.04	1.4784	4.88	1.4664	5.05	1.4750
9	5.1	1.498	5.14	1.4920	5.14	1.4764	5.06	1.4789
10	6.7	1.499	5.11	1.5018	5.20	1.4837	5.02	1.4849
11	4.8	1.502	5.34	1.5091	5.17	1.4882	5.15	1.4903
12	3.7	1.506	4.92	1.5128	5.23	1.4910	7.10	1.4933
13	2.9	1.509	5.27	1.5167	5.34	1.4928	4.64	1.4963
14	1.9	1.514	5.12	1.5191	4.30	1.4942	3.1	1.4983
15	1.8	1.512	5.18	1.5211	5.62	1.4980	7.3	1.4994
16	1.7	1.513	5.18	1.5218	3.31	1.5023	3.2	1.5012
17	1.4	1.513	5.13	1.5224	3.5	1.5040	2.8	1.5024
18	1.4	1.515	4.90	1.5253	1.1	1.5080	5.5	1.4970
19	2.4	1.507	2.3	1.5268	3.7	1.5102	3.9	1.4970
20	2.4	1.504	2.1	1.5288	4.9	1.5106	4.1	1.4969
21	1.6	1.510			6.0	1.5110		
22	1.4	1.514						
23	2.0	1.517						
24	1.9	1.516						
25	2.2	1.512						
26	1.9	1.513						
27	1.4	1.513						
28	4.4	1.508						
29	5.9	1.505						
Total	98.60		96.60		98.77		96.93	

Note: R.I. @ 20°C.

Table 6-C

Tabulation of Adsorption Analyses Results

Sample No.	G-133		G-133-P		G-137		G-137-P	
	Ml.	R.I.*	Ml.	R.I.*	Ml.	R.I.	Ml.	R.I.
1	5.03	1.4930	5.10	1.4662	5.01	1.4762	4.94	1.4611
2	5.14	1.4910	5.35	1.4619	5.22	1.4697	5.20	1.4599
3	5.43	1.4870	5.12	1.4597	5.24	1.4700	5.41	1.4587
4	5.45	1.4790	5.18	1.4590	5.17	1.4720	5.12	1.4589
5	5.36	1.4760	5.09	1.4589	5.15	1.4720	5.19	1.4620
6	4.87	1.4764	5.01	1.4601	5.10	1.4814	5.13	1.4678
7	5.22	1.4782	5.00	1.4658	5.26	1.4892	5.02	1.4744
8	5.06	1.4811	5.47	1.4762	5.23	1.4897	5.14	1.4830
9	5.17	1.4843	5.02	1.4798	5.11	1.4974	5.09	1.4889
10	4.98	1.4870	5.07	1.4848	5.16	1.5004	4.84	1.4940
11	5.48	1.4892	4.72	1.4909	5.22	1.5029	5.43	1.4997
12	5.07	1.4880	4.89	1.4965	5.60	1.5048	5.04	1.5023
13	5.13	1.4710	4.6	1.4998	5.29	1.5084	5.08	1.5070
14	5.32	1.4620	4.2	1.5004	5.41	1.5108	5.11	1.5152
15	5.28	1.4526	3.6	1.5031	5.32	1.5098	4.95	1.5200
16	5.09	1.4443	2.8	1.5065	5.02	1.5128	5.47	1.4968
17	8.70	1.4418	4.0	1.5032	2.3	1.5158	5.13	1.4642
18	4.98	1.4397	4.8	1.5025	3.8	1.5144	9.76	1.4591
19			6.7	1.5011	6.7	1.5047	1.10	1.4448
20			7.1	1.5002			0.90	1.4430
Total	96.76		98.82		96.31		99.06	

Note: *R.I. @ 40°C. All others at 20°C.

Table 6-D

Tabulation of Adsorption Analyses Results

Sample No.	S-100-F		S-100-F-P	
	Ml.	R.I.	Ml.	R.I.
1	4.85	1.5171	5.04	1.4970
2	4.88	1.5150	6.45	1.4805
3	5.13	1.5124	6.00	1.4728
4	5.17	1.5028	4.99	1.4728
5	5.32	1.5030	4.63	1.4747
6	5.17	1.5008	4.92	1.4793
7	5.18	1.5022	4.94	1.4873
8	5.23	1.5057	5.24	1.4940
9	5.41	1.5069	4.99	1.5027
10	5.14	1.5090	4.96	1.5080
11	5.23	1.5098	5.36	1.5013
12	5.48	1.5090	4.97	1.5158
13	3.3	1.5113	5.27	1.5169
14	5.0	1.5022	4.90	1.5190
15	3.1	1.5133	4.82	1.5135
16	15.6	1.4763	3.1	1.5200
17	8.4	1.4790	2.3	1.5200
18			3.3	1.5183
19			2.8	1.5183
20			8.4	1.5183
Total	97.40		97.38	

Note: R.I. @ 40°C.

Table 6-E

Tabulation of Adsorption Analyses Results

Sample No.	G-125		G-128		G-134	
	Ml.	R.I.*	Ml.	R.I.	Ml.	R.I.*
1	5.00	1.5009	5.00	1.4510	5.20	1.4998
2	5.36	1.4783	5.16	1.4508	5.01	1.4962
3	5.11	1.4689	4.94	1.4506	5.41	1.4960
4	5.06	1.4686	4.83	1.4504	5.05	1.4960
5	5.14	1.4686	5.04	1.4504	5.14	1.4950
6	4.97	1.4719	5.21	1.4502	5.17	1.4900
7	4.96	1.4780	5.01	1.4502	5.70	1.4888
8	5.06	1.4841	5.30	1.4500	5.04	1.4880
9	5.05	1.4922	4.91	1.4539	5.32	1.4878
10	5.11	1.4922	5.05	1.4631	5.12	1.4899
11	5.19	1.5056	5.04	1.4780	5.16	1.4920
12	5.08	1.5090	5.08	1.4967	5.32	1.4938
13	5.36	1.5128	5.17	1.5100	5.02	1.4950
14	5.10	1.5088	6.10	1.5113	5.11	1.4983
15	8.80	1.5050	5.01	1.5120	4.90	1.4983
16	4.10	1.5035	6.10	1.5152	4.30	1.5035
17	2.60	1.4978	8.50	1.5158	5.10	1.5037
18	2.80	1.5274	4.90	1.5190	5.00	1.5028
19	3.10	1.5300	2.70	1.5223	4.50	1.5022
20	4.30	1.5280			2.70	1.5022
Total	96.95		99.05		99.27	

Note: *R.I. @ 40°C. All others @ 20°C.

BIOGRAPHICAL ITEMS

James Hubert Gary was born November 18, 1921, in Victoria, Virginia. He was graduated from Victoria High School in June, 1938, and entered the Virginia Polytechnic Institute in September of that year. He was graduated with honors in June, 1942, receiving the Bachelor of Science in Chemical Engineering degree. After graduation he served as an officer with the Anti-Aircraft Artillery of the Army of the United States in the South West Pacific Theatre. Upon return to inactive duty, he entered the graduate school of the Virginia Polytechnic Institute in October, 1945, and was granted the degree Master of Science in Chemical Engineering in September, 1946. Upon graduation, he became employed in the Technical Service Division of the Standard Oil Company (Ohio) at Cleveland, Ohio. In September, 1948, he entered night school at the Case Institute of Technology and continued his graduate studies there until June, 1949. In September, 1949, he was granted a leave of absence from the Standard Oil Company (Ohio) and entered the University of Florida to undertake graduate studies leading to the degree of Doctor of Philsophy. He is a member of Phi Lambda Upsilon, Phi Kappa Phi, Tau Beta Pi, and the American Chemical Society, a junior member of the American Institute of Chemical Engineers, an associate member of Sigma Xi, and a Registered Professional Engineer in the State of Ohio.

This dissertation was prepared under the direction of the Chairman of the candidate's Supervisory Committee and has been approved by all members of the Committee. It was submitted to the Graduate Council and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Date June 11, 1951

Dean T. M. Simpson

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